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THE

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BY

EDWARD L. NICHOLS, ERNEST MERRITT,
AND FREDERICK BEDELL

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THE

PHYSICAL REVIEW

INFRA-RED EMISSION SPECTRA.[1]

By William W. Coblentz.

THE present experimental investigation was performed in the Physical Laboratory of Cornell University during the academic year 1904–1905. It forms the second part of an investigation of infra-red radiation, rendered possible by a grant from the Carnegie Institution of Washington. The first grant was for "Investigating infra-red emission and absorption spectra." Finding it impossible to complete the work in the time allotted, the Institution very generously renewed the grant, and the writer takes this opportunity to express his gratitude for the assistance rendered. In the Physical Laboratory he is under deep obligations to Professors E. L. Nichols and E. Merritt for advice and criticisms as well as for the numerous facilities placed at his disposal. His dealings with the two institutions have been so agreeable that it is with a feeling of regret that additional phases of the work could not be continued with them.

The present investigation deals with the question of the distribution of emission lines (bands) in the infra-red, especially with the question of presence of lines beyond $1.5\,\mu$. All the infra-red lines predicted by our spectral series formulæ end in the short wavelength just beyond the red. Any information as to the presence of lines beyond this point will aid in establishing these formulæ upon

[1] Extracts from a memoir on this subject submitted to the Carnegie Institution of Washington for publication.

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a firmer, less empirical basis than they have at present. From our knowledge of the radiation from the "black body," which is most intense in the region of 1.2 μ to 2.5 μ at high temperatures, one would expect the emission bands at 2 μ, if there be any, to be just as intense as those found by Snow[1] at 1 μ. Other points of interest which developed as the work progressed will be noted in their proper places.

All observers agree in thinking that when radiation is emitted by a gas, in one case by heating it, and in another case by sending an electric current through it, the mechanism which is brought into play must differ in some important respects in the two cases. The present work deals with the radiation from a gas when a current is sent through it.

The work divides itself into two parts, viz., emission spectra of the arc between metallic electrodes and of the chlorides of the alkali metals in the carbon arc; and emission spectra of gases in vacuum tubes. The contrast between these two forms of radiators is worthy of notice. The arc is noted for its enormous heat radiation in proportion to its light radiation. On the other hand the vacuum tube radiates but little heat. Consequently, in the study of these two kinds of radiators, the form of the device for exploring their spectra must differ. If a radiometer is used the period must be short, for the arc, to avoid heating of the window and the consequent shifting of the zero reading. This, however, is of less importance than the variation in intensity of the radiation from the arc which requires a recording instrument having a short period.

For the vacuum tube a much greater sensitiveness must be used, which means a longer period for a linear radiometer vane. Fortunately the radiation from the vacuum tube is uniform, which permits the use of an instrument having a slow period.

In the present work a Nichols radiometer, a 7 cm. rock-salt prism and a 35 cm. focal length mirror spectrometer were used.[2]

For the emission spectra of the metals, the radiometer vanes had an area of about 2 × 15 mm. each, and the short period was due to

[1] Snow, PHYS. REV., 1, p. 35, 1893.

[2] Described in the PHYS. REV., 16, pp. 35 and 77, 1903, and in "Infra-red Investigations," Washington, D. C. Published by the Carnegie Institution, October, 1905.

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the heavy fiber suspension. The vacuum tube radiation being very weak, required great sensitiveness, which was obtained in part by reducing the size of the vanes (of mica) to 1 × 10 mm. and selecting a fine fiber. The behavior of such a vane is entirely different from a heavier one. At low pressures the vane before the window was suddenly repelled from it, due apparently to the radiation from the window. This repulsion occurred when both vanes were black, and when the unexposed one was not covered with lamp-black. It was not due to electrification, and throughout the vacuum tube work it was necessary to use a torsion head to keep the deflection on the scale.

I. Infra-red Emission Spectra of Metals.

This work was begun by examining the spark spectra of such metals like Zn, Al and Cu. An induction coil and condenser were used. No emission lines could be detected; instead of lines a weak continuous radiation was detected in the region of 2 μ to 3 μ, which appeared to be due to the hot particles from the electrodes. The arc between metallic electrodes of Fe, Zn and Cu was then tried; but no lines could be detected in the region of 1 μ, beyond which point the incandescent oxides gave such an intense continuous, "black body," spectrum that the emission lines would have been obliterated by the radiation from the oxides. The vapors from the copper arc had but little "black body" radiation. No emission lines were detected, however, although several have been predicted in the region of 2.5 μ.

In the Zn arc the oxides are formed so rapidly that it is almost impossible to work with this metal. The problem then is to separate the black body radiation of the oxides from that of the vapors, which is very different from the work in the visible spectrum.

Chlorides of Metals.

The chlorides of Na, Li and K were then examined in the carbon arc, using for the purpose hollow carbon electrodes filled with the salt. The carbons used varied from 6 to 9 mm. in diameter, the holes being from 1.4 to 2.5 mm. A direct current of 15 amp. from a 104-volt circuit was used. The radiometer slit was reduced

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to 0.1 mm. in width, nevertheless the radiation at 2 μ, which at the most gave a deflection of only a few millimeters was not resolved into individual lines. This is in marked contrast with the strong emission lines at 1 μ, and as will be noticed later on, the continuous radiation at 2 μ would blot out any weak emission lines, as far as a radiometer or a bolometer is concerned. Here a photographic process would be better since the effect upon the plate is cumulative, and one would have dark lines superposed upon a dark background, just as Abney and Festing[1] found for their absorption spectra at 1 μ.

Carbon Arc.

In Fig. 1 is given the emission spectrum of the carbon electrodes, curve *a*, and that of the violet vapor of the arc, curve *b*. It will be noticed that there is but little radiation from the vapor except a

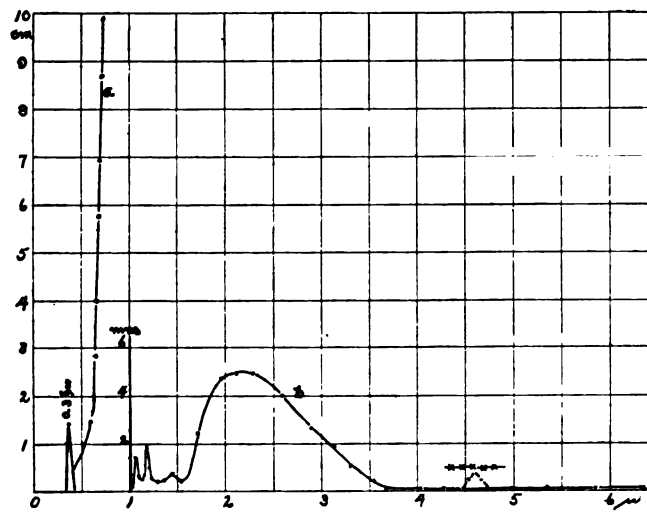

Fig. 1. Carbon arc; *a* = electrodes, *b* = vapor.

slight amount from 2 μ to 3 μ. On the other hand the deflection was thrown off the scale for the radiation from the electrodes, just beyond the red. Snow[2] found the radiation from the arc vapors concentrated in a single line, in the violet, at 0.385 μ. This line is four times as intense as the one at 1.09 μ. In the present work

[1] Abney and Festing, Phil. Trans., 177, p. 887, 1882.
[2] Snow, PHYS. REV., 1, p. 35, 1893.

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the lines are of about equal intensity, due in part to the loss of intensity of the violet line, caused by the radiometer window. A new line occurs at 1.2 μ, while on a thorough reëxamination no line was found at 4.52 μ. This is of considerable interest since it shows that no CO_2 is formed, and that the electrodes are consumed in a different manner. They do not disappear in the ordinary form of combustion. There is but little residue from mechanical disintegration; they disappear chiefly in the form of vapor. The absence of radiation from the carbon vapors is in marked contrast with the radiation from the electrodes, any trace of which, as already mentioned, was sufficient to cause large deflections. The black body radiation is not very intense at a low temperature and the maximum lies beyond 3 μ. The oxides in the arc have a high temperature; the maximum lies at 2 μ and the weak radiation in this region is to be attributed to the low density of the vapors.

Sodium, Na.

Snow (*loc. cit.*) found that the salts of the metals gave the same emission lines as the metal itself, and that the chlorides were well adapted for emission spectra work, using hollow carbon electrodes.

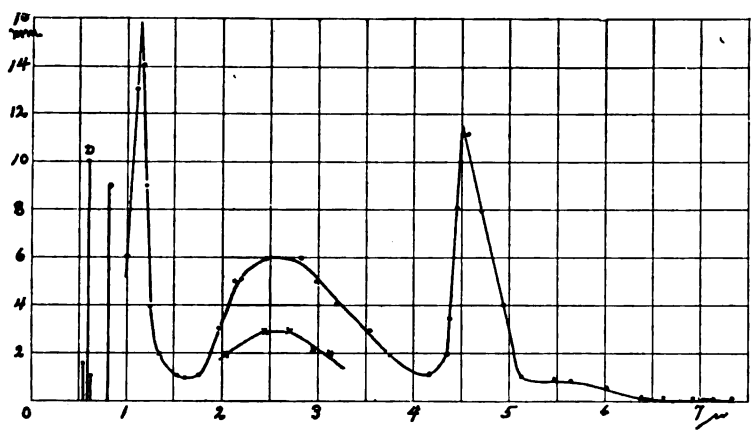

Fig. 2. Na.

For this reason only the chlorides of the metals were used. The present work was not concerned with the verification of his results, which were used only in comparing the relative intensity of the lines

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investigated. He used a quartz prism, which on account of its larger dispersion permits a greater accuracy in determining wave-lengths. In the present work the question was whether there are lines beyond the region investigated by him. The distribution of the energy in the vapor of Na is shown in Fig. 2.

Snow found the intensities of the lines at 0.589 μ, 0.818 μ and 1.13 μ to have a ratio of 87 : 66 : 42. In other words the energy in 0.589 μ is more than twice that of the line at 1.132 μ. In the present work the intensities of these two lines are exactly reversed, and in the same proportion. Since the dispersion is smaller this may be due to the impurity of the spectrum.

From 2 μ to 3 μ there is a weak continuous radiation, which appears to be due to the oxides of the metals in the arc.

For Li this is not so intense, and, since the solid material (dust) coming from the arc is also less, the evidence is strengthened in favor of the emission at 2 μ to 3 μ being due to oxides. The emission band at 4.52 μ is also to be noticed. Since it occurs only

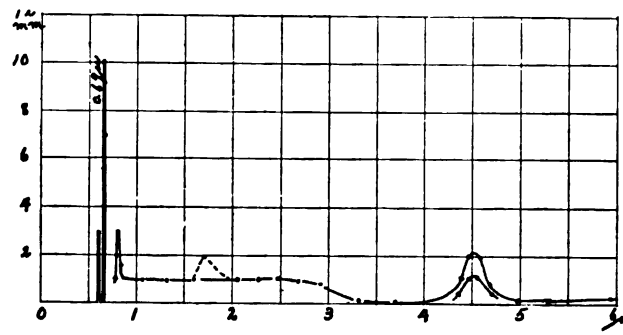

Fig. 3. Li.

when the salts of the metals are in the arc, and is *not* to be found in the carbon arc its source remains undetermined. If it be due to CO_2, from the air, then from the shifting of the maximum to the longer wave-lengths (found by Paschen, *loc. cit.*, being at 4.40 μ for the bunsen flame) it would appear that the temperature of the arc is about 4,000° absolute.

Lithium, Li.

The chloride of lithium vaporizes so easily that no true measure of the radiation from the dense vapor could be obtained. In like

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manner the radiation from the oxides at 2 μ to 3 μ is also weak. The bands at 0.67 μ and 0.811 μ (Fig. 3) have the same ratio of intensity as found by Snow. Beyond this point no lines could be detected, except a slight band at 4.52 μ.

Potassium, K.

In Fig. 4 is shown the emission curve of potassium. The KCl does not vaporize so easily as LiCl and is readily adapted to the arc. Snow found strong lines at 0.768 μ, 1.155 μ and 1.22 μ, the first one being four times that of the band at 1.15 μ. In the present work the last two lines were not not quite resolved and no comparison can be made. The band at 1.47 μ was also found by Snow. The usual region of continuous radiation is found from 2 μ to 3 μ. The 4.52 μ emission band is strong. The emission band of CO_2 at

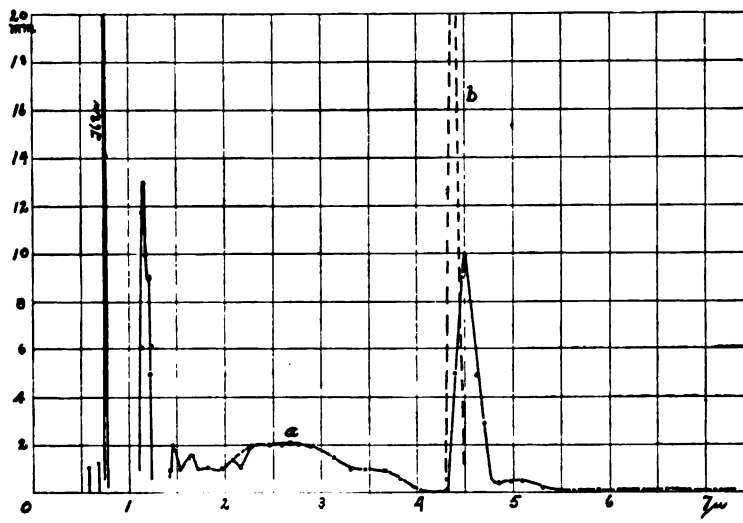

Fig. 4. Potassium ; b = Bunsen flame.

4.40 μ, using a bunsen burner, is also given, curve b, — the latter is three times (deflection equals 3.2 cm.) as strong as the band at 4.52 μ.

As a whole from these curves it will be noticed that no emission lines occur beyond 2 μ, which is entirely unexpected. Beyond this point a weak emission line would be obliterated by the continuous spectrum. The band at 4.52 μ will be noticed shifted to 4.75 μ

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in the vacuum tube radiation. The intensity of the emission lines found depends upon the density of the metallic vapor in the arc. From the fact that no lines were observed beyond those found by Snow it is not to be inferred that no lines lie beyond 2μ. The work simply shows that, for the conditions which produce the lines at the end of the red, no lines of measurable intensity are to be found beyond this point. It is true that Lehmann[1] has just shown that Rb and Cs have lines at 1.7μ; but the emission curves of these two elements, found by Snow, also show *weak* lines in this region, and it is only the cumulative effect upon the phosphor-photographic plate that has enabled Lehmann to map them.

II. Infra-red Emission Spectra of Gases in Vacuum Tubes.

Since the incandescent oxides in the arc and spark emit a continuous spectrum of sufficient intensity to obliterate any weak emission lines, beyond 2μ, it is impossible to detect them. The vacuum tube lacks these defects, and is adapted to this work provided one has sensitive apparatus to detect the radiation emitted.

The dispersed infra-red radiation from gases in a vacuum tube is of considerable interest in comparison with the radiation of gases in a flame. The work of Julius[2] and of Paschen[3] shows that by mere temperature elevation gases emit characteristic discontinuous spectra. From a theoretical standpoint such an investigation is also of importance, since all the infra-red lines predicted by our spectral series formulæ end in the short wave-lengths just beyond the red. This presents the interesting question whether emission lines are to be found beyond the region of 2μ. In this connection a recent theoretical paper by Garbasso[4] is to be noticed in which he maintains that the series of Kayser and Runge have a real existence.

In the preliminary part of this work the vacuum tube used by Drew[5] was employed. In this tube the electrodes were at right angles to and at a short distance from the main part which formed the positive column. Several rubber joints were in series with the

[1] Lehmann, Phys. Zeit., 5, 823, 1904.
[2] Julius, Licht u. Wärmestrahlung verbrannter Gase, Berlin, 1890.
[3] Paschen, Ann. der Physik., 3, 53, p. 334, 1894.
[4] Garbasso, Nuovo Cimento, 9, p. 113, 1905.
[5] Drew, PHYS. REV., 17, p. 321, 1903.

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mercury pump, McLeod gauge and the vacuum tube. Several gases were examined, all of which, except hydrogen, showed an emission band in common at 4.75 μ. Hoping to gain intensity of the radiation, a tube was made similar to one used by Runge and Paschen.[1] The aluminum electrodes were 2.5 cm. long, and 2.8 cm. diameter, through which the radiation passed axially into the spectrometer slit of 8 mm. length and 1 mm. width. The radiometer slit was 0.7 mm. The internal diameter of the main portion of the vacuum tube was 1 cm. and its length was from 15 to 18 cm. The window was of rock salt secured on the outside by means of bees-wax covered with shellac varnish. The window was also secured by means of shellac which had been boiled until it thickened. To avoid rubber joints the vacuum tube was sealed to the pump and the gases introduced through a barometric column of mercury. The tube was air tight but, at a low pressure, it would become so hot that vapors would be given off and the cathode luminescence would disappear. This luminescence would reappear after the tube had cooled. According to Travers (Study of Gases), this is due to gases absorbed by the electrodes. At any rate it did not interfere with the work, since the tube was used at such a pressure that it did not become heated. All evidence indicated that the impurity band at 4.75μ, which was found in all the gases in the preliminary work was due to something that entered with the gas; and it was finally shown to be due to contamination with CO_2 while making the gas. The problem then was to make a gas which was free from even slight traces of CO_2. Previous experience showed that to bubble a gas through several purifying solutions in series with the pump was not sufficient. Hence, in preparing such a gas like CO, an ordinary mercury gas pipette was used. The gas was washed back and forth from the mercury pipette, through a tube containing P_2O_5 into a pipette of KOH, for about half an hour, to free it from CO_2 and to dry it. After such a treatment nitrogen and oxygen did not show the impurity band at 4.75 μ.

The residual gas in the pump and glass connecting tubes was swept out by passing a discharge through it and heating it from the outside.

[1] Runge and Paschen, Astrophys. Jour., 3, p. 4, 1896.

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A large Charpintier and also a Max Kohl No. 4 induction coil were used to excite the vacuum tube. For convenience, for most of this work, the primary was connected directly through a rheostat to a 104 volt, 60 or 120 cycle, alternating current.

An ammeter was placed in the primary circuit, while an a. c. millivoltmeter having a resistance of 21,760 ohms was used to measure the current in the secondary.

The primary current varied from 3 to 6 amp., and the secondary from 0.012 to 0.028 ampere.

Since the spectrometer arm was movable, the vacuum tube had to be adjusted before the slit, by hand. The points on the curves given are usually the mean of several readings.

Observations were made for constant current in secondary and variable pressure, and also for constant pressure and variable current.

The method of observation consisted in obtaining the radiometer deflection for the gas when the discharge was passing and then, after stopping the discharge, allowing the deflection to return towards its original zero reading. The hot cell would prevent the deflection from returning to the original zero in 50 seconds (radiometer period) and the difference in the two zero readings gave approximately the deflection due to the hot cell. Another method for finding the deflection due to the hot cell consisted in passing the discharge for 50 seconds, then on stopping the discharge and raising the shutter reading the deflection. Of course the cell cools somewhat while obtaining the deflection, but it is not a great amount in comparison with the total deflection. Since the cell became heated the least at 0.6 to 1 mm., it was used at this pressure. In the region up to 1.5 μ *no* radiation from the hot cell could be detected. Beyond 3 μ, for a pressure of 0.6 to 1 mm., the deflections often amounted to several centimeters. On the other hand nitrogen shows strong lines at 1 μ which would indicate that if nitrogen emits bands on account of its thermal condition, then it must be at a *higher temperature* than the cell.

Water Vapor, H_2O.

After finding the impurity band at 4.75 μ in all the gases except hydrogen, and knowing that water has an absorption band at this

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point, a special attachment was provided to introduce water into the previously exhausted pump and vacuum tube.

The emission spectrum was found for various pressures, up to 3 mm., but no emission bands were found. On the contrary, the hot cell, after stopping the discharge, gave deflections which were as large as those for the vapor. With water vapor the cell became much hotter than for the other gases.

A slight trace of water vapor has a great effect in depressing the intensity of the emission lines as was found on allowing air to enter the tube; and only after filling the tube several times with air and exhausting it did the air lines, at 0.9 μ, 1.05 μ and 4.75 μ, appear in their usual intensity.

It will be noticed that the water vapor has *no* emission lines, which is true of the vapor in a bunsen or oxyhydrogen flame. On the the other hand alcohol vapor shows quite a strong emission spectrum from 2 μ to 3 μ. This is probably due to the difference in density of the two vapors.

Hydrogen, H.

This sample of hydrogen was generated from Zn + HCl and dried in H_2SO_4 and in P_2SO_5.

In the region of 1 μ energy is radiated which may be due to slight traces of nitrogen. *No* emission band is to be found at 4.75 μ. The radiation curve for the hot cell (observations plotted in circles) coincides with that of the gas.

Oxygen, O.

The first sample of oxygen, made by heating $KClO_3 + MnO_2$, showed the impurity band at 4.75 μ and no further examination was made of it.

A sample of electrolytic oxygen was then taken from the large generator and washed in KOH and dried over P_2O_5 on glass wool. Two examinations were made, on different days, but *no* emission band could be detected at 4.75 μ. In the region of 1 μ no deflections greater than 1.5 mm. were recorded. As a whole the gas showed *no* emission lines for the region examined, which was to 5 μ, This is of considerable interest in what follows on CO and CO_2, where there is a strong emission line at 4.75 μ.

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Carbon Dioxide, CO_2.

This gas was made from $KClO_3 + H_2SO_4$ and dried in P_2O_5. It was found that there are *no* emission lines until we arrive at 4.75 μ.

The current through the gas varies with the pressure. An examination of the 4.75 μ band was made for constant current and variable pressure, the current being 0.02 ampère. The results are shown in Fig. 6, which will be discussed in connection with CO, and it will be sufficient to add that the gas was first put into a pipette of phosphorus to remove the oxygen which was present. Starting with a sample of this gas at 1 mm. pressure, and adding oxygen until the pressure was 3.7 mm., no change could be detected in intensity of 4.75 μ the band which would indicate that if the band be due to CO then the CO_2 is already dissociated when starting. Occasionally a dark ring or dark patches would appear on the inside of the constricted portion of the vacuum tube. It would suddenly disappear and then reappear elsewhere. Whether it was due to carbon in the tube or to the dissociation of CO_2 remains undetermined.

Warburg's work[1] shows that the temperature of the axis of the tube is much higher for nitrogen than for hydrogen, so that traces of CO_2 in nitrogen ought to become the hotter. It was noticed that the 4.75 μ band occurring as an impurity, was most intense in nitrogen, which, if the same amount of CO_2 was present in each gas, would indicate that the N was the hotter.

Carbon Monoxide, CO.

The CO was made by heating oxalic acid, $C_2H_4O_2$, and conc. H_2SO_4 and passed through a KOH solution into a pipette of KOH. The generating flask was then replaced by a mercury gas pipette and a tube of P_2O_5 on glass wool, and the gas was then washed back and forth through the P_2O_5 for a long time. This sample showed no water vapor lines at low pressures. The emission curves of CO are in Fig. 5, where curve *a* is for a pressure of 0.3 mm. and *b* for a pressure of 0.8 mm. There seems to be a slight trace of radiation throughout the spectrum but *no* strong emission lines are to be found except the one at 4.75 μ.

An examination of this band was made for a constant current of

[1] Warburg, Ann. der Physik. (3), 34, p. 265, 1895.

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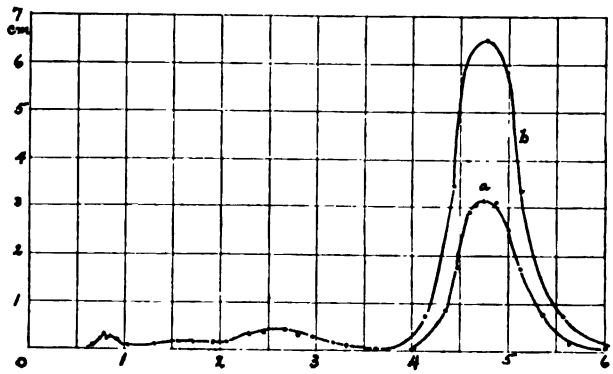

Fig. 5. CO ; $a = 0.3$ mm. pressure, $b = 0.8$ mm. pressure.

0.02 amp. and variable pressure. The results are given in Fig. 6, in which the abscissæ are pressures in millimeters of mercury, and the ordinates are deflections in centimeters. It is to be noticed that

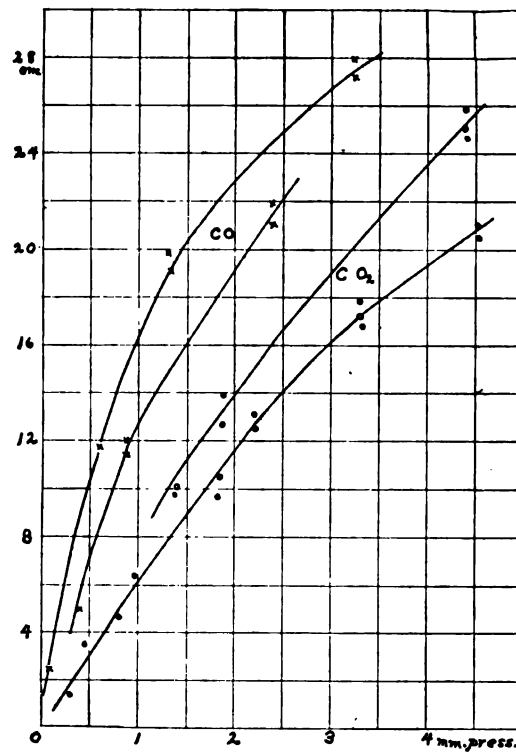

Fig. 6. CO and CO_2 band at 4.75 μ. Variation in intensity with pressure.

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the intensity of the CO band is much greater than that of CO_2 for *all* pressures, the current of 0.02 amp. being the same for both gases. Moreover the intensity does not pass through a maximum as is true of the H and N lines lying near the visible spectrum. The greater intensity of the CO would make it appear as though the 4.75 μ band were due to this gas.

Ethyl Alcohol, C_2H_5OH.

Ordinary absolute ethyl alcohol was used. It was introduced into the previously exhausted pump, through an especially provided bulb and stopcock. The emission curve, Fig. 7, is very un-

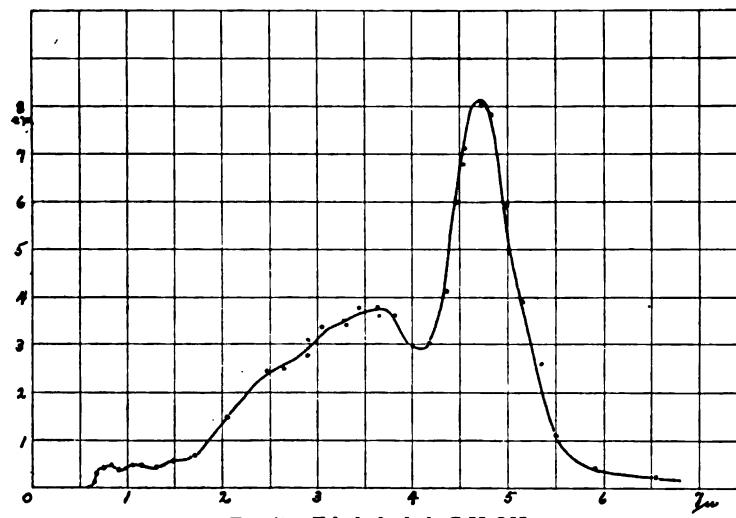

Fig. 7. Ethyl alcohol, C_2H_5OH.

usual. It shows no distinct lines except the strong band at 4.75 μ which is to be found only in CO and CO_2. The continuous spectrum from 2 to 4 μ is difficult of explanation. Possibly it is a composite of bands of alcohol vapor equivalent to the water vapor bands found in the bunsen flame. In the latter, however, the bands are in groups with regions of zero radiation. The bands at 4.75 μ indicate a dissociation of the alcohol vapor into H (red line) and CO_2 or CO, just as ammonia shows the nitrogen bands.

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Nitrogen, N.

The first sample of nitrogen examined was made by heating a saturated solution of equal parts of sodium nitrite, $NaNO_2$, and ammonium chloride, NH_4Cl, washed in KOH and dried in H_2SO_4 and in P_2O_5.

The emission spectrum of this sample of N is given in Fig. 8, curve *b*. In addition to strong lines just at the end of the red we have the usual band at 4.75 μ which is unusually intense. In fact,

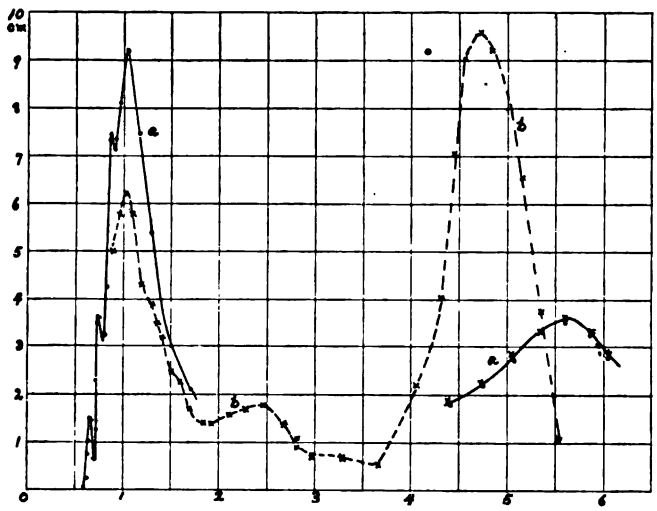

Fig. 8. Nitrogen ; *a* = atmospheric nitrogen.

for a pressure of 5 mm. the deflections from this band were from 30 to 35 centimeters.

One difficulty in making nitrogen by this method is that the oxides are also formed. The presence of the 4.75 μ band showed that it is due to CO_2 or traces of N in CO or CO_2. The problem then was to prepare a small quantity of nitrogen which was free from oxides of nitrogen, and also free from O and CO_2. The presence of a trace of an inert gas like helium did not enter the question of the origin of the 4.75 μ band. Hence atmospheric nitrogen was most serviceable. To this end a glass tube containing P_2O_5 on glass wool was connected in series with a gas pipette containing a strong KOH solution and a pipette containing sticks of red phosphorus under water. The phosphorus of course was used to re-

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move the O, while the KOH removed the CO_2. The air was washed back and forth for some time. The KOH pipette was then replaced by a mercury gas pipette, and the gas was washed back and forth for about half an hour to dry it and remove the last traces of oxygen.

The result is shown in curve *a* of Fig. 8, which is of no small significance, especially in the region of 4.75 μ where *no band* is to be found. The curve (dots and crosses) shows that the radiation from the gas and from the hot cell is of equal intensity. The decrease in the intensity, thus forming an apparent maximum at 5.5 μ is due to the fact that in moving the spectrometer arm the vacuum tube was not adjusted before the slit, hence the last two readings are for the radiation from the side of the tube instead of its axis.

In the final work the gases were not studied in the order given here, the CO_2 and CO coming last. The absence of the 4.75 μ

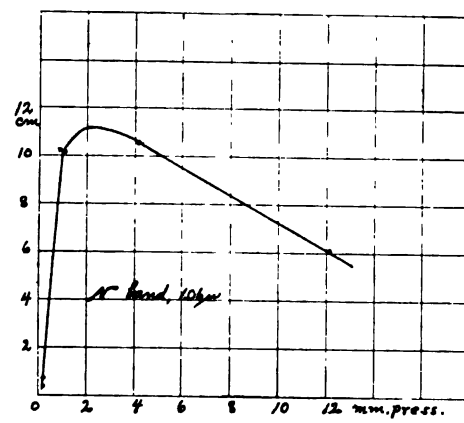

Fig. 9. Variation in intensity with pressure of the nitrogen band at 1.06 μ.

band in N and NH_3 excluded the possibility of its being due to nitrogen. Several drops of water were introduced into the gas, but no change could be detected in the radiation at 4.75 μ showing that this band is not due to water vapor. Hence it remained to be shown whether it is due to CO_2 or CO.

In discussing those two gases it was shown that the radiation from CO is much stronger than for CO_2 at 4.75 μ.

The presence of strong emission bands just beyond the red hav-

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ing maxima at 0.66 μ, 0.75 μ, 0.90 μ and 1.06 μ was found only in nitrogen. Helium [1] is the only other gas known which has strong lines (bands) in this region, and from the scanty data at hand it appears as though this property were confined to the inert gases.

A study was then made of these emission bands under constant current and variable pressure and *vice versa.* In Fig. 9, is given the curve of the 1.06 μ band for variable pressure (current const. 0.02 amp.) which is the ordinary gas conduction curve of the visible spectrum. Ordinates are deflections in centimeters, abscissæ are

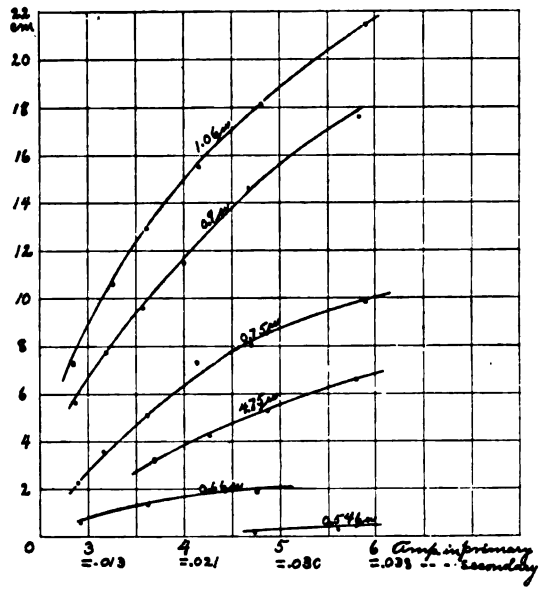

Fig. 10. Variation in intensity of the nitrogen bands with current.

pressures in millimeters. The maximum lies at about 2 mm. which agrees well with observations in the visible spectrum.

In Fig. 10 are given the emission curves of the bands at 0.546 μ, 0.667 μ, 0.75 μ, 0.90 μ, 1.06 μ and 4.75 μ, keeping the pressure constant at 1.4 mm. and varying the current.

All the curves agree in showing that the intensity (plotted as ordinates) increases with increase in current in the secondary, which agrees with Langenbach,[2] and with Ferry [3] for the visible spectrum.

[1] Runge and Paschen, Astrophys Jour., 3, p. 4, 1896.
[2] Langenbach, Ann. der Phys. (4), 10, p. 789, 1903.
[3] Ferry, PHYS. REV., 7, 1, 1898.

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Several large Leyden jars were used in parallel with the vacuum tube when the intensity of the radiation increased due to an increase in the current through the tube.

Ammonia, NH_3.

The ammonia used was made by heating $NH_4Cl + KOH$ (solid) and passing the gas through tubes of CaO which had been heated for several hours. These tubes were heated while starting, to expel the air. The first sample was examined just after the C_2H_5OH, and from the appearance of the curve, Fig. 11, some of

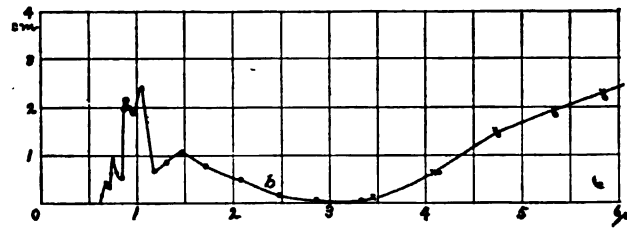

Fig. 11. Ammonia, NH_3.

the latter vapor must have been present. The second sample, made with greater precautions, did not show any radiation beyond 2.5 μ. In the region of 4.75 μ, the observations for the radiation from the hot cell and the gas (indicated by crosses) coincide. The nitrogren bands at 0.75 μ, 0.9 μ and 1.06 μ are due to the dissociated NH_3.

Radiation From a Vacuum Tube When Heated Externally.

The very different behavior of the 4.75 μ band from those at the end of the red made it highly desirable to learn whether it can be due to the mere rise in temperature of the gas. If it obeys Kirchoff's law, it cannot be more intense than the black body radiation at the same temperature. The radiation of the hot glass cell beyond 3 μ, when hot (at cathode-ray pressure) gave deflections that were comparable with that of the 4.75 μ band. This would lead one to think that the 4.75 μ band is due simply to rise in temperature of the gas. On the other hand, in the region of 1 μ the hot cell gave *no* appreciable deflections, while the gas, nitrogen, gave *strong* emission bands, which would indicate that if these emission bands

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be due to a pure thermal excitation, following Kirchoff's law then the temperature of the gas must be very high as compared with that of the cell walls. The problem then was to find the radiation from the vacuum tube when heated externally to the temperature it had during the electrical discharge, which is really the black body radiation; also to find the radiation from a black body, *e. g.*, a Leslie cube, whose temperature can be quite accurately determined.

In order to determine the radiation from the vacuum tube when externally heated, the part between the electrodes was wound with an iron wire through which an electric current was passed. The walls of the tube were heated to the temperature they generally had during the electrical discharge at very low pressure. The tube was filled with air and with CO_2, and the radiation was found for *all pressures* up to atmospheric. The deflections were thrown entirely off the scale for *all* pressures for the region of 4.75 μ, hence this region of the spectrum was not explored for emission bands. This indicates an intensity of radiation several times that from the vacuum tube during the passage of the discharge. Although the ends of the tube were not hot, when heated externally, the tube is analogous to the black body. Whether or not it is entirely analogous is not of the chief importance. Its radiation was several times as intense as that from the electrically excited tube, which was the question to be answered. Whether or not the emission band at 4.75 μ is due to thermal excitation, due merely to a rise in temperature, or to electrical excitation is undetermined. The experiment shows that since its intensity is less than that of a black body, it is not untenable to consider it to be due to a rise in temperature of the gas.

But this is not a sufficient criterion for udging the quality of the radiation. One objection is that the selective emission at 4.75 μ ceases immediately after the electrical discharge ceases, which is not true of the externally heated tube. Warburg (*loc. cit.*) has shown from theoretical considerations that after the discharge ceases it requires only a small fraction of a second for the gas to assume its original temperature.

In this connection it is well to notice Paschen's[1] work on the emission of CO_2, when heated in a metal tube, also when passed

[1] Paschen, Ann. der Physik. (3), 53, p. 26, 1894.

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through a coil of sheet platinum 4 cm. long, 3 mm. internal diameter, heated electrically.

He found the radiation of the 4.4 μ band of CO_2 for columns 7 cm. and 33 cm. long. The 7 cm. column behaved like a layer of infinite thickness, *i. e.*, the intensity of the emission of this wave-length is proportional to the intensity of radiation of a black body for the same wave-length and temperature. In Fig. 12, curve *b* represents the emission of the 4.4 μ band of CO_2, for a tube 7 cm. long when heated by means of a bunsen burner from 100 to 500°. In this same figure curve *c*, also due to Paschen, shows the emission

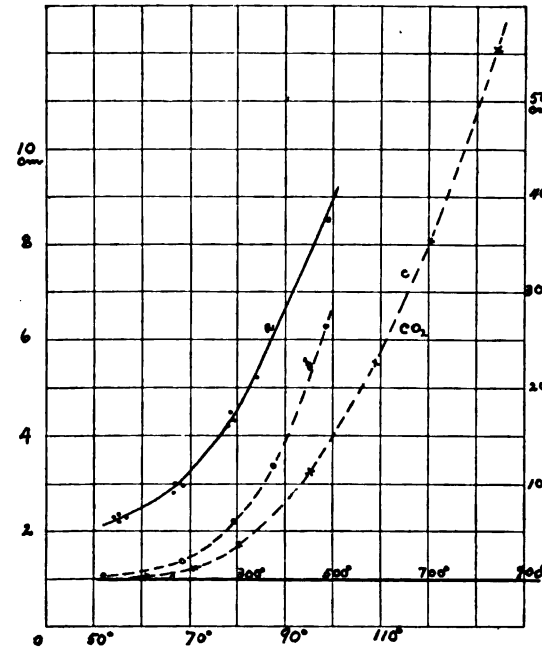

Fig. 12. Radiation from a black body at 100° C., curve *a*; curves *b* and *c* = radiation from CO_2. (Paschen.)

of the 4.4 μ band of CO_2 when heated by passing the gas through a coil of platinum which was heated electrically.

The temperature of the gas was observed by means of two thermopiles, the first one being placed at the point where the gas issued from the orifice; the second one being placed about one centimeter above this point. Both curves show the very rapid increase in intensity of the emission lines with rise in temperature.

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RADIATION FROM A BLACK BODY WHEN HEATED TO 100° C.

Since the temperature of the cell could not be determined accurately it was highly desirable to compare its radiation with that of a solid whose temperature could be varied and determined more accurately. To this end the radiation from a thin-walled, blackened copper vessel was found when filled with water which was heated electrically. The escaping vapors from the hot water caused such a variation in the temperature of the room that the radiometer became very unsteady, hence only the region of 4.75 μ was examined. In Fig 12, curve *a* gives the emission curve of this vessel for different temperatures of the water. The curve is very similar to those found by Paschen. Of course, the temperature of the outside of the vessel is less than that of the water, but not sufficient to debar a comparison with the hot vacuum tube. Mention has already been made of the fact that the constricted part of the vacuum tube is the hotter at high pressures, while the regions surrounding the electrodes are the hotter at low cathode-ray pressures. At the latter pressure the deflections for the hot cell were from 8 to 10 cm. The vessel of hot water, under similar conditions gave a deflection of 8.5 cm. for a temperature of about 96°.

At a temperature of 70° the deflection is about 3 cm.

As a whole the results show that the radiation from the cell walls is due to a rise in temperature which is not much, if any, greater than that of the vessel containing water. The temperature of the gas in the vacuum tube is an entirely different question which must be considered separately.

The fact must not be overlooked that the radiation from the vacuum tube gave large deflections simply because of the great sensitiveness of the instrument and not on account of the actual intensity as compared with the deflections from gases in a Bunsen flame. In the latter the deflections for the 4.4 μ CO_2 band were some 60 to 70 cm. for the old instrument, so that in the present work the deflections would be 50 times as great, viz., 3,000 cm. In other words, in the vacuum tube curves the deflections are only from $\frac{1}{250}$ to $\frac{1}{3000}$ as great as from the bunsen flame, and the Nernst heater.

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TEMPERATURE OF GAS IN THE VACUUM TUBE.

Warburg's theoretical work (*loc. cit.*) on the temperature of the vacuum tube has already been mentioned. He showed that the temperature of nitrogen is much higher than that of hydrogen.

The intensity of the 4.75 μ impurity band in nitrogen, for all pressures, was so much greater than for all the other gases that one is led to think that it is due to the higher temperature of the gas.

Wood [1] gives data from the observed mean temperature of gases in a vacuum tube for different pressures, and currents of 0.001 to 0.003 ampere. In all cases the computed and observed temperatures are in fair agreement, the observed values being slightly less than Warburg's values, as one would expect, from the use of a thermopile which cannot be made infinitely thin. The observed values fall upon a straight line, which shows the accuracy of the observations. Using these values and extrapolating to a current of 0.02 ampere, in the present work, for a pressure of 1.8 mm. of nitrogen this would indicate a temperature of about 250° C. while for a pressure of 3 mm. the temperature of the axis would be about 325°. For a current of 0.025 ampere the temperature would be 300° and 400° respectively.

The whole shows that for the large currents used in the present work (0.02 to 0.028 amp.) it is not unthinkable that the 4.75 μ band is due to the heating of the residual gas. On the other hand, the black body at 325° C. does not emit a very perceptible radiation at 1 μ while the emission lines of N in this region are very intense. They indicate a very much higher temperature, some 4000° abs., if we consider the maximum of the envelope of the curve, drawn through the highest points of these emission lines, which maximum lies just beyond the red. This reasoning leads to the result that the gas is at two distinct temperatures, which is hardly the case. If the gas had this high temperature then one would expect the cell walls to grow hotter. Electrical excitation suggests itself, which brings us to a theoretical consideration of the phenomena of vacuum tube radiation.

THEORETICAL.

It remains for us to consider the theoretical side of this subject. Experimental observations always have some value. This is not

[1] Wood, Ann. der Physik. (3), 59, p. 238, 1896.

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always true of theories which are built, more or less, upon hypotheses and must stand or fall with them. For example, nowadays one no longer considers spectra to be due to molecular or atomic vibrations; the divisibility of the atom into smaller electrically charged particles, called "ions" or "corpuscles" must be assumed to account for observed facts. The foremost and most conservative in propounding such a theory is J. J. Thomson.[1] J. Stark[2] is more daring in that he classifies these "ions," and gives the functions that each class has to perform.

Before considering these theories it will be well to distinguish between several forms of radiation, since everybody gives out some form of radiation, in the form at least of heat waves of great wavelength. If a body can give out radiation continuously without changing its nature it is called a *pure thermal* radiation. If it cannot continue to give out this radiation indefinitely, without changing its nature, even when the temperature is kept constant (*e. g.*, fluorite which emits light on heating) then the radiation is termed *luminescence*. The vacuum tube is thought to give out light by "*electro-luminescence*."

The vacuum tube is always quite cool in comparison with the arc. This brings us to the question of "temperature." What do we mean by the temperature of a body, particularly with the two forms of radiation just mentioned. Both emit light, nevertheless, if we were to heat a piece of iron until it felt as hot to the touch, or until the mercury in a thermometer expanded to the same height, as it does for the vacuum tube, we know from ordinary experience that the iron would not emit light. "Temperature" is something we are supposed to measure by ordinary means. The word itself is used carelessly and is an endless source of discussion. To anticipate a little what is to follow — Stark uses the terms "thermal and electrical temperature." The purely "*thermal temperature*" for any one gas is proportional to the mean square of the *molecular* speeds. The "*electrical temperature*" is proportional to the mean square of the *ionic* speeds. In a strong electrical field, *e. g.*, spark electrodes, the ionic velocities will be distributed in a very different

[1] Thomson, Conduction of Electricity Through Gases, Chaps. 13 to 16.
[2] Stark, Elektricität in Gasen.

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manner from that prescribed by the Maxwell-Boltzmann Law, and the "electrical temperature" may differ very widely from the "*thermal.*" The arc is a region of high thermal and low electrical temperature; the spark has a low thermal and a high electrical temperature.

To return to the theory, there is considerable evidence for believing that the chemical atom or molecule is composed of positively and negatively charged particles called ions. These oppositely charged particles are equal in amount since the molecule as a whole is electrically neutral. It is possible to separate from the molecule a minute particle which carries a negative charge, and thus leave an equal positive charge on the remainder of the molecule. This state of affairs is brought about whenever an electric field is produced, as for example, the difference of potential between the terminals in the carbon arc, of the spark gap in the secondary of an induction coil, or of the electrodes of a vacuum tube. Under the influence of an electric field these dissociated particles are set in motion. Beside their ordinary gas motion, there will be a component along the length of the tube (in a vacuum tube) produced by the electrical forces. Although the charges are the same, the negative ions, the electrons, on account of their small mass will acquire a great speed, and by collision with neutral molecules will give rise to fresh ions. The energy acquired however will be the same for both since they move through the same difference of potential. The mean free path of the electron will be the greater since it is smaller in size. The mean energy at collision, in any case, will be that acquired by the charged particle in moving through its path under the action of electrical forces. When the electron collides with a molecule several effects will be produced. The first is to increase the kinetic energy of the molecule as a whole, which in turn by colliding with other molecules, will cause a rise in the thermal temperature of the gas. As a result the electrons in the molecules will be thrown out of their positions of equilibrium and will execute a series of vibrations. In so doing they will emit radiation in the form of heat or light, depending upon the intensity of the excitation, which in turn depends upon the temperature.

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When an electron collides with a molecule the second effect is an acceleration of the former, which, when properly interpreted, means a wave motion, hence periodicity (Stark, *loc. cit.*). This period will be determined by the time of impact, independently of the chemical nature of the body. Since all possible times of impact are possible, an infinite number of different electromagnetic waves will be emitted, and we have a continuous spectrum. This is for the free electrons. The electrons that remain bound in the molecule will also be set into vibration by the impact of the collision. Since they are thus bound, there will be a relative motion among them, and the period of any one or group of these electrons will be characteristic of the kind of atom. The line and band spectra of the elements are, from this standpoint, due to these electrons within the atom.[1] In a more recent paper on tnis subject by Nutting,[2] the recombination of these dissociated aggregates is emphasized as being the source of line spectra.

For this second effect the energy increases with the potential gradient, since the radiation from the gas is caused by the collisions between molecules and electrons, which latter are moving with high speeds. As already mentioned in the high temperature radiation, where the collision is between molecules, the energy increases with the temperature. The electrical temperature distribution will be different from the thermal, and Kirchoff's law for the relation between emission and absorption will not hold for radiation from a gas in a vacuum tube. The spectral distribution of intensity will be a function of the velocity distribution of the electrons. The greater the number of electrons with high speed in a volume element, the more will the intensity maximum be shifted towards the short wavelengths.

For this reason the cathode glow is blue, since the cathode fall is about 300 volts. On the other hand in the position column, where the fall is only about 30 volts, the light emitted is red for nitrogen. According to Stark's (*loc. cit.*) computations in which the kinetic energy is equated to the temperature, this would indicate an electrical temperature of some 6000° for the cathode glow.

[1] Stark, Ann. der Phys. (4), 14, p. 506, 1904.
[2] Nutting, Astro. Phys. Jour., 21, p. 400, 1905.

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The ionic energy[1] (the minimum kinetic energy) necessary to disrupt an atom is in the order, metals, Hg 8 (volts), H, N (27 volts) and O. From this it would follow that if we mix H with N the fall of potential and the electrical temperature of the positive column will be changed. The temperature will be increased if the gas to be added has a higher ionic energy, *e. g.*, N to Hg or N to H (Heuse,[2] Herz). This will be of interest in comparing the relative intensities of the 4.75 μ band of CO_2 when it occurs as an impurity in N (very intense) and in O or NH_3 where it is weak.

These views will now be briefly considered in connection with the results obtained in the present research.

Prior to this investigation on vacuum tube radiation only one type of selective emission of gases in the infra-red had to be accounted for, viz., emission bands of water vapor and CO_2. They were thought to be due to thermal temperature of the gas. However, the data bearing upon this subject are so scarce that writers, in referring to them, generally expressed their opinions rather cautiously. Some have vaguely intimated that it might be something similar to luminescence in the visible spectrum — call it thermalescence.

From the present research on the intensity of the infra-red emission bands of N and CO_2, for constant current and varying pressures, and *vice versa*, it becomes evident that we have to deal with two distinct types of radiation, the one being represented by the 4.75 μ band of CO and CO_2, the other being represented by lines of N at 0.90 μ and 1.06 μ. The 4.75 μ band of CO and CO_2 behaves in an entirely different manner from all the rest. Its intensity increases with increasing pressure (for constant current) of the gas, but never reaches a maximum, becoming asymptotic at 5 to 6 mm. pressure.

On the other hand, the other bands increase in intensity with increase in pressure (for constant current), become a maximum at about 2 mm. pressure, and then decrease in intensity with a further increase in pressure, which agrees with observations in the visible spectrum.

All lines increase in intensity with increase in current, as found in the visible spectrum.

[1] Herz, Ann. der Phys. (3), 54, p. 244, 1893.
[2] Heuse, Verh. d. d. phys. Ges., 1, 269, 1899.

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Condensers in parallel with the vacuum tube caused a slight increase in the intensity of the lines, due to an increase in the current through the tube. This is due to the well known fact that on account of the high self-induction of the coil, the discharge of the condenser takes the easier path through the vacuum tube. The whole shows that the bands of N, (He), and H, near the visible spectrum, are related to the visible bands, while the 4.75 μ band is of an entirely different type.

Returning to the theory, it is interesting to recall Ångström's [1] predictions in regard to the mechanism which produces these radiations. As noticed elsewhere, he found that the total radiation *increases*, while the luminous radiation *decreases* with increase in pressure of the gas, and concluded that there is a "regular" and "irregular" radiation present during the electrical discharge. This would tend to change the efficiency of the vacuum tube, as found by Ångström and by Drew.

In the present work, the *decrease* in infra-red radiation (4.75 μ band) and the simultaneous *increase* in the visible radiation, with decrease in pressure, explains very clearly the rise in efficiency of vacuum tubes. It also explains why the total radiation passes through a minimum as observed by Ångström and by Drew (*loc. cit.*).

In connection with the theoretical work just mentioned the behavior of these two types of radiation may be explained in the following manner: Consider the lines in and near the visible spectrum. At high pressures the electrons will not attain a high speed on account of the numerous neutral molecules, and their freedom of motion will be limited. At a lower pressure their freedom of motion will be greater, the number of collisions will be more frequent, the ionization will increase and the electrical temperature [2] which is proportional to the mean square of the ionic speeds will attain a maximum. At a still lower pressure, on account of the scarcity of the molecules, there will be fewer collisions in a given time, the ionization will decrease and the "electrical temperature" will decrease.

On the other hand this explanation will not account for the behavior of the 4.75 μ band which appears to be due to a thermal

[1] Ångström, Ann. der Physik. (3), 48, p. 493, 1893.

[2] Stark, Elektricität in Gasen, from consideration of the kinetic energy of the electron computes an electrical temperature of some 6000°.

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radiation, excited by the collision of electrons with the neutral gas molecules. The gas molecule as a whole will suffer an increase in its kinetic energy, and, in colliding with other molecules, will cause a rise in the thermal temperature of the gas. With increase in pressure, *i. e.*, in the number of gas molecules, the number of collisions will increase, the intensity of the thermal radiation will increase but will not pass through a maximum, as is true of the other bands, because a stage will be arrived at where there will be a decrease in the ionization and in the collisions of the molecules. At still higher pressures the gas would cease to conduct the current.

Aside from these theoretical considerations, there is some experimental evidence for believing that the 4.75 μ band is of thermal origin. First, the gas must be hotter than the tube, for during the passage of the current the radiation tangential to the axis of the tube is probably different from the longitudinal, and the cell walls assume the mean temperature of the gas only after the current has passed for some time. It has already been shown under the discussion of the temperature of the gas in the vacuum tube, that the mean thermal temperature is from 300° to 400° C., depending upon the current and the pressure. It was also shown there that the black body at these temperatures did not emit a perceptible radiation at 1 μ, while the emission lines in this region are very intense, indicating a temperature of perhaps 4000° abs. On the other hand the "black body" at 4.75 μ radiated almost as intensely as the vacuum tube. This would indicate two distinct temperatures, which is hardly the case.

Second, the distribution of the heat in the vacuum tube is very different for different pressures. At a high pressure the constricted portion of the vacuum tube is the hotter while at low pressure it is quite cool, and the region surrounding the electrodes is the hotter.

Third, the emission increases with the pressure (equivalent to an increase in the thickness of the emitting layer) and approaches a limiting value. Paschen (*loc. cit.*) has found for CO_2 at atmospheric pressure, in a brass tube heated by a bunsen burner that a column 7 cm. long emitted and absorbed energy just as strong as a column 33 cm. long. In the present case the 15 cm. column of CO_2 at 5 mm. pressure is equivalent to a column 1 mm. long at 760 mm.

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pressure. This is not a very long column of the gas as compared with Paschen's, nevertheless, judging from the behavior of the small traces of CO_2 in air, it does seem impossible for it to emit radiation as intense as that observed at 4.75 μ. This would require a very high temperature. If the shifting of the CO_2 band toward the long wave-lengths continues with the rise in temperature for the region beyond 4.4 μ, just as Paschen (*loc. cit.*) found for the region preceding 4.4 μ, then the 4.75 μ band would indicate a temperature of some 6500° to 7000° (found by extrapolating from Paschen's values). This is close to Stark's (*loc. cit.*) "electrical temperature" of 6000° for the cathode glow. Returning to the strong emission lines just at the end of the red, if we consider the maximum of the envelope (the curve) drawn through the highest points on these emission lines, which maximum lies just beyond the red, then, from the "displacement law" $\lambda_{max.} T =$ const., the thermal temperature appears to be about 4000° abs.

From this line of reasoning it would appear that we can consider the 4.75 μ band and the bands at the end of the red to be due to a high thermal condition in the vacuum tube, without having recourse to an "electrical temperature."

The continuous spectrum of alcohol vapor would indicate a higher temperature than that found by bolometric measurements. But even here the evidence is contradictory when compared with the emission of water vapor which showed no emission spectrum at 2.8 μ, where the bunsen flame has emission lines.

Evidently further investigation is needed to elucidate this subject — and such an investigation is in progress.

Summary.

The present investigation of infra-red emission spectra had for its aim the study of the region of the spectrum lying beyond 2 μ, which heretofore had never been examined. The question of the presence of emission lines beyond this point is chiefly of theoretical interest.

Two classes of radiation have been investigated, viz., the arc between metallic electrodes and the chlorides of the alkali metals in the carbon arc, and the discharge through a vacuum tube using different vapors and gases.

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It was found for the arc between metal electrodes, that the oxides emitted a black body spectrum of sufficient intensity to obliterate any emission lines if any were present.

Using the chlorides of the alkali metals, the strong emission lines mapped by Snow were verified, but beyond 2μ *no* emission lines could be found.

The emission spectra of the following vapors and gases were examined in a vacuum tube; H_2O, C_2H_5OH, H, N, NH_3, CO and CO_2. Of this number the C_2H_5OH, CO_2 and CO have a very strong emission band at 4.75μ.

Nitrogen is the only gas studied which has strong emission lines in the infra-red. The maxima are at 0.75μ, 0.90μ and 1.06μ. The behavior of these lines is entirely different from the 4.75μ band found in CO_2 and CO. At a constant current the intensity of the 4.75μ band increases with the pressure but never reaches a maximum, becoming asymptotic at 5 to 6 mm. pressure. On the other hand the nitrogen bands increase in intensity with increase in pressure, become a maximum at about 2 mm. pressure, then decrease in intensity with a further increase in pressure, which agrees with observations in the visible spectrum.

At a constant pressure all lines increase in intensity with increase in current, as found in the visible spectrum.

Condensers in parallel increased the intensity slightly, due to an increase in the current through the tube.

The aim in using a vacuum tube was to avoid oxides. No lines, however, were found beyond 2μ, except the 4.75μ band which seems to be due to the warming of the gas. Since the intensity of the vacuum tube radiation is only from $\frac{1}{250}$ to $\frac{1}{3000}$ as great as that of a black body, if there be weak emission lines beyond 6μ it would be almost impossible to detect them with our present measuring instruments.

The emission spectrum of C_2H_5OH shows that a vapor in a vacuum tube can emit a continuous spectrum.

BUREAU OF STANDARDS,
WASHINGTON D. C., Aug., 1905

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THE EQUAL ARM BALANCE.

By H. V. Carpenter and Zella E. Bisbee.

THE static equations of the balance have been worked out in a variety of forms depending upon the completeness with which the errors of the construction are taken into account. It was the purpose of this investigation to determine the value of the constants in these equations for balances of common types, in order that the equations might be reduced to the simplest form that would represent the true conditions. The equation of equilibrium of the balance to be sufficiently complete must be one which expresses the state of the balance under all conditions of load, sensitiveness, and rigidity of the beam. The formulæ given here were worked out with this end in view, and have been carefully checked experimentally to show the values of the constants involved and to determine how closely the theoretical conditions are fulfilled by the balances in use. In order to secure the most satisfactory experimental check the general equation of equilibrium derived below was placed in such a form that it expressed the sensitiveness of the balance as a function of the load upon the pans.

Derivation of the General Equation of Equilibrium.

The discussion which follows is based upon the following statements:

1. The inequality of the arms is so small that it may be neglected. It rarely exceeds .01 per cent. and so while it must be considered for accurate weighing it is not appreciable in the mechanical behavior of the balance.

2. The knife edges in a satisfactory balance are so thin that their thickness may be neglected except possibly for very sensitive conditions of the balance. This was tentatively assumed and is borne out by the experimental results which are given.

3. Since all readings of the deflection of the beam are taken with

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the beam stationary or by an equivalent method, the center of mass of each pan with its stirrup and load may be taken as always exactly beneath its supporting knife edge and no effect would be produced on the behavior of the balance if the mass of each pan with its stirrup and load were concentrated at its supporting knife edge.

4. Any load added to the pans will cause a downward distortion of the beam with a consequent lowering of the end knife edges and of the center of gravity of the beam. The experiments show the magnitude of this effect.

5. The line joining the center of gravity of the beam with the central knife edge is assumed to be perpendicular to the straight line joining the end knife edges. This condition is always very closely approached in the ordinary adjustment of the balance, and

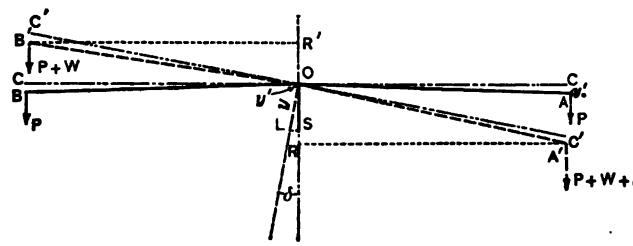

Fig. 1.

any ordinary error in it would not appreciably affect the behavior of the instrument.

Since each pan with its load may be considered as having its center of gravity at its knife edge, we may treat the two as acting together at a point half way between the two knife edges, that is at a point directly below (or above) the central knife edge as indicated in Fig. 1. Distances downward are considered as positive and distances upward as negative.

Let O = central knife edge.

P = mass of one pan and stirrup.

e = excess weight.

$OA = OB = OA' = OB' = l$, the length of each arm.

B = mass of beam.

W = load on one pan.

γ_0 = distance of the center of gravity of beam below O, with pans empty.

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y_0' = distance of the effective center of gravity of pan system above or below O, with pans empty.

$\bar{y}_0$ = distance of the center of gravity of entire moving system below O with pans empty.

Since any distortion of the beam due to added weights in the pans will be proportional to the weights added we can write $OL = y = y_0 + KW$, where y is the distance the center of gravity of the beam lies below O for the load W grams in each pan, and K is the increase in y due to one gram increase in W. Similarly $A'C' = y' = y_0' + K'W$ where K' is the distance the end knife edges are lowered by 1 gram increase in each pan. K' will always be larger than K.

Now from the law of moments,

$$B \cdot LS + (P + W)B'R' = (P + W + e)A'R, \qquad (A)$$

$$< COC' = < LOS = \delta$$

and

$$< A'OC' = < B'OC' = \sin^{-1}\left(\frac{y_0' + K'W}{l}\right)$$

$$= \cos^{-1}\frac{\sqrt{l^2 - (y_0' + K'W)^2}}{l}.$$

$$\therefore < OA'R = < COA' = < COC' + < C'OA'$$

$$= < \delta + \sin^{-1}\left(\frac{y_0' + K'W}{l}\right).$$

Likewise

$$< B'OC = < \delta - \sin^{-1}\left(\frac{y_0' + K'W}{l}\right).$$

Then

$$B'R' = l\cos\left[\delta - \sin^{-1}\left(\frac{y_0' + K'W}{l}\right)\right],$$

$$LS = y\sin\delta = (y_0 + KW)\sin\delta,$$

$$A'R = l\cos\left[\delta + \sin^{-1}\left(\frac{y_0' + K'W}{l}\right)\right],$$

and equation A becomes

$$B\sin\delta(y_0 + KW) + (P + W)l\cos\left[\delta - \sin^{-1}\left(\frac{y_0' + K'W}{l}\right)\right]$$

$$= (P + W + e)l\cos\left[\delta + \sin^{-1}\left(\frac{y_0' + K'W}{l}\right)\right],$$

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$$B \sin \delta(y_0 + KW) + (P + W)l\left\{ \cos\left[\delta - \sin^{-1}\left(\frac{y_0' + K'W}{l}\right)\right]\right.$$

$$\left. - \cos\left[\delta + \sin^{-1}\left(\frac{y_0' + K'W}{l}\right)\right]\right\} = el \cos\left[\delta + \sin^{-1}\left(\frac{y_0' + K'W}{l}\right)\right],$$

$$B \sin \delta(y_0 + KW) + (P + W)l\left\{ 2 \sin \delta \left(\frac{y_0' + K'W}{l}\right)\right\}$$

$$= el\left[\cos \delta \frac{\sqrt{l^2 - (y_0' + K'W)^2}}{l} - \sin \delta \left(\frac{y_0' + K'W}{l}\right)\right].$$

$$B \sin \delta(y_0 + KW) + (P + W)2 \sin \delta(y_0' + K'W)$$

$$= el \cos \delta \frac{\sqrt{l^2 - (y_0' + K'W)^2}}{l} - e \sin \delta(y_0' + K'W),$$

$$\sin \delta[B(y_0 + KW) + 2(P + W)(y_0' + K'W) + e(y_0' + K'W)]$$

$$= el \cos \delta \frac{\sqrt{l^2 - (y_0' + K'W)^2}}{l}$$

Since a balance will not work satisfactorily if y_0' exceeds .01 cm. and K' in the balance having the most flexible beam of any tested had a value of .0001, it will be seen that $(y_0' + K'W)^2$ is negligible as compared with l^2 and $e(y_0' + K'W)$ is so small in comparison with $2(P + W)(y_0' + K'W)$ that the equation takes the form

$$\tan \delta = \frac{el}{(yB_0 + KW) + 2(P + W)(y_0' + K'W)}. \qquad \text{(I.)}$$

The above equation may also be derived more directly as follows, making the same approximations as in the formula above.

$$\bar{y}_0 = \frac{\Sigma My}{\Sigma M} = \frac{By + 2(P + W)y'}{B + 2(P + W)} = \frac{B(y_0 + KW) + 2(P + W)(y_0' + K'W)}{B + 2(P + W)}.$$

Suppose the addition of a small weight e to one pan causes a steady deflection δ of the system. The weight e will cause a moment in one direction of $el \cos(\delta + < A'OC')$ equaling closely $el \cos \delta$. The restoring moment due to the deflection of the beam will be

$$[B + 2(P + W)]\bar{y}_0 \sin \delta,$$

so for equilibrium

$$[B + 2(P + W)]y_0 \sin \delta = el \cos \delta,$$

or

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$$\tan \delta = \frac{el}{B(y_0 + KW) + 2(P + W)(y_0' + K'W)}. \qquad \text{(I.)}$$

Tan δ is proportional to the number of divisions deflection of the pointer, so if the excess weight, e, be taken as constant, δ and W are the only variables and the sensitiveness for different values of the load may be calculated if the constants are known. In other words it is an equation for the curve of sensitiveness of any balance.

Examination of the equation brings out the following points most of which are familiar:

1. The deflections of the pointer will be directly proportional to the difference between the loads.

2. If other things could be kept constant the sensitiveness would be proportional to the length of the beam, $2l$; for a beam of given shape however, an increase in l will cause an increase in B, or K and K', or all. The additional fact that a long beam vibrates too slowly leads makers to make the beam as short as the convenient arrangement of the pans will permit.

3. Unless the beam is very rigid and y_0' very small the mass of the pans may cause as great a decrease in the sensitiveness of the balance as the mass of the beam, further than this, the mass of the pans has a very much greater effect upon the period of vibration of the balance than the mass of the beam since the pans are farther from the center of oscillation. It is not uncommon to find balances with pans much heavier than necessary while the beam is carefully made rigid and light.

4. The balance will remain stable so long as the denominator of the fraction is a positive quantity, so either y_0 or y_0' may be negative, that is either the center of gravity of the beam or the effective center of gravity of the pan system may be above the central knife edge and still the balance may work properly.

It was found that in short beams of the common high truss type, the bending under load was too small to be detected or K and K' are negligibly small for this important class of balances; this gives us the simpler relation,

$$\tan \delta = \frac{el}{By_0 + 2(P + W)y_0'} \qquad \text{(II.)}$$

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If $y_0' = 0$, or the knife edges are in the same plane,

$$\tan \delta = \frac{el}{By_0} \qquad \text{(III.)}$$

or the sensitiveness is constant for all loads.

If y_0' is positive an increase of load will decrease the sensitiveness for all values of W.

If y_0' is negative the sensitiveness will increase with the load until, when $By_0 < 2(P + W)y_0'$, the balance will be unstable.

Short beam balances are commonly sent out by the makers with the end knife edges slightly below the central one. There are two reasons for this:

(1) Such a balance will weigh light bodies with greater accuracy than heavy ones, which is usually desirable. (2) A heavy body balanced in the pans increases the moment of inertia of the system greatly, but if it decreases the sensitiveness at the same time the period of swing may not be much changed.

The condition giving constant sensitiveness is very desirable since it enables weighings to be made by interpolation with great rapidity but it is very difficult to adjust the balance to this condition.

In the case of long or slender beam balances that will bend enough under load to effect their behavior, if y_0' is positive the sensitiveness will decrease as the load increases more rapidly than it would if the beam were rigid. If y_0' is negative, we have the interesting case in which as the load is increased, the sensitiveness rises at first, possibly to infinity, and then as the effect of the bending of the beam becomes greater the sensitiveness will decrease. This may be understood by giving y_0' a negative value in equation I.

$$\tan \delta = \frac{el}{B(y_0 + KW) + 2(P + W)(y_0' + K'W)}.$$

As W increases the denominator will decrease at first and then increase, reaching a minimum value and causing a maximum value of $\tan \delta$ at the value

$$W = -\frac{2y_0' + 2PK' + BK}{4K'},$$

an expression which increases with the negative value of y_0', and

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which can be shown to be a load less than half great enough to bring the knife edges to the same plane. If y_0' is not very small the value of W for maximum sensitiveness may be greater than the capacity of the balance as determined by the safe load of the knife edges, in which case the sensitiveness would increase with the load throughout or it might reach infinity within the limit of the balance.

The experimental work was taken up to see first, whether or not the equations as given are sufficiently complete and accurate; second, to determine the value of the constants in the equations for the balances used.

The first balance used was one listed by Queen & Co. as "Analytical Balance, No. 1," built for a capacity of 200 gr. The beam is made of aluminum, strongly braced and weighs 84.2 gr.; the

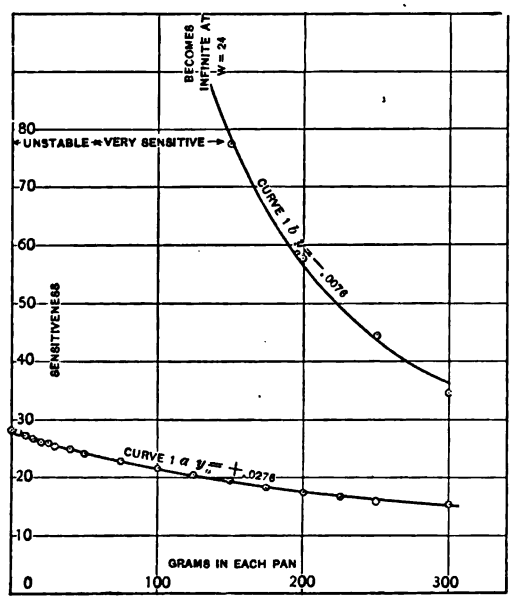

Fig. 2.

length of each arm is 7 cm. The end knife edges are each set in a brass block which is clamped in place in a slot in the beam by means of four set screws. The height of the knife edges can be adjusted by inserting pieces of paper of varying thicknesses under the brass blocks. Great care was necessary in adjusting them, however, since each knife edge must be maintained parallel to the central one.

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Before any change was made in the adjustment of the knife edges, curves of sensitiveness were determined for two positions of the bob which controls the center of gravity of the beam. The values obtained are tabulated in Table I. and plotted in Fig. 2.

TABLE I.

Formula II. $\tan\delta = \frac{el}{By_0 + 2(P+W)y_0'}$. $l = 7$ *cm.* $e = .01$ *gr.* $P = 59.1$ *gr.*

$B = 84.2$ *gr.* $\tan\delta = .000918d$. $y_0' = +.00385$ *cm.* I*a*, $y_0 = +.0276$.

Load in Grams.	Deflections = d		Load in Grams.	Deflections = d	
	Observed.	Calculated.		Observed.	Calculated.
− 59	36.3		40	24.8	
− 42	33.5		50	24.1	24.2
− 32	31.9		75	22.8	
− 22	30.8		100	21.5	21.5
0	27.9	27.6	125	20.3	
5	27.7		150	19.4	19.4
10	27.0		175	18.2	
15	26.5		200	17.4	17.7
20	26.2		225	16.8	
25	25.8		250	16.0	
30	25.3		300	15.1	15.0
I*b*, $y_0 = -.0076$ *cm.*					
24		infinite	200	57.5	56.5
35	infinite	953.0	250	44.2	43.8
150	77.8	78.6	300	34.4	36.0

In all the curves given the points are experimental values while the curves are drawn to represent the theoretical values which are also tabulated. After considerable experimental work had been completed, it was found that with this balance the bending of the beam could not be detected so that formula II. represents the behavior within the limits of accuracy attained in the experiments.

In formula II.,

$$\tan\delta = \frac{el}{By_0 + 2(P+W)y_0'},$$

we have the following values: $l = 7$ cm., $e = .01$ gr., $P = 59.1$ gr., $B = 84.2$ gr. and $\tan\delta = .000918d$, where d is the deflection of the pointer of the balance in scale divisions as tabulated. This leaves the constants y_0 and y_0' to be determined by Least Square adjust-

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ment. This was done using values from table I*a* and the most probable values of y_0 and y_0' were found to be $y_0 = +.0276$ and $y_0' = +.00385$ that is the center of gravity of the beam was .0276 cm. below the central knife edge and the plane of the end knife edges was .00385 cm. below the same line. Using these values and various values of W in (II.), the theoretical values given were found and are represented by the curve I*a*. The close agreement of the experimental and theoretical values throughout the range given shows simply that formula II. with proper constants represents satisfactorily the behavior of the balance for this particular adjustment throughout the entire range of load.

The next step was to increase the sensitiveness by raising the bob. This change will effect formula II. only by changing y_0, so if the actual change in y_0 can be determined experimentally, the formula should give the new curve of sensitiveness with no further change. The change in y_0 was determined as follows: The beam with the bob weighed 84.2 gr., the bob weighed 11.6 gr., the pitch of the screw carrying the bob was .0285 cm. The bob was raised a known number of turns and so an accurately known distance, then the change in y_0 is equal to the change in the position of the bob multiplied by the ratio of the mass of the bob to the mass of the beam and bob.

In this case y_0 was decreased .0352 cm., thus raising the center of gravity of the beam from .0276 cm. below O to .0076 above or $y_0 = -.0076$ cm. Using this value of y_0 and the previously determined value of y_0' the values given in table and curve I*b* were calculated. Experimentally, the balance was unstable until a load of 35 gr. was added and was so sensitive throughout the entire range that the determinations were very difficult. The close agreement between the calculated and experimental values here gives stronger proof that the formula is sufficient. It should be noted however, that the formula gives indifferent equilibrium at $W = 24$ gr. while the experiments show that the balance is not stable until W is greater than 35 gr. The uncertainty of the balance as the unstable condition is approached, indicates that the thickness of the knife edges is affecting its behavior.

The next step was to raise the end knife edges by placing under

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them a bit of paper. It was found impossible to get the change in y_0' by measuring the thickness of the paper before inserting it, because it was impossible to tell how hard the oblique clamping screws pressed the knife edge block down upon the paper, and as there were always three or four thicknesses of paper under the knife edge block, its effective thickness could only be approximated.

The end knife edges were raised approximately .0147 cm. above their former position and curves were determined for three positions of the bob giving the data in Table II. The theoretical curve *2a* was determined from formula II. by adjustment as before, y_0 being found to be + .0483 and y_0' — .00965. Curves II*b* and II*c* were calculated by using the same value of y_0' and correcting y_0 according to the known change of the bob as before; y_0 being equal to .0679 in II*b* and .0955 in II*c*. These curves show the entirely different behavior of the balance when the end knife edges are higher than the central knife edge. The close agreement between observed and calculated values shows that formula II. is sufficient.

TABLE II.

Formula II. $\tan\delta = \dfrac{el}{By_0 + 2(P + W)y_0'}$. $l = 7$ *cm.* $e - .01$ *gr.* $P = 59.1$ *gr.* $B = 84.2$ *gr.* $y_0' = -.00965$. II*a*, $y_0 = +.0483$.

Load in Grams.	Deflections. Observed.	Deflections. Calculated.	Load in Grams.	Deflections. Observed.	Deflections. Calculated.
− 42	20.5		50	37.8	38.7
0	26.4	26.0	75		51.5
25		31.1	100	78.1	76.2
II*b*, $y_0 = +.0679$.					
0	16.8	16.6	100	29.1	28.7
25	18.26		150		45.3
50	20.4		200		106
75	24.5				
II*c*, $y_0 = +.0955$.					
0	11.15	11.08	100	16.3	15.9
25		11.9	150		19.05
50		12.85	200	25.2	25
75		14	300		68.6

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Several adjustments of the knife edges were made in the attempt to bring them all into one plane in order to check formula III., but without entire success. The best result is given in Table III. and curve III., Fig. 4, where, although the balance was quite sensitive,

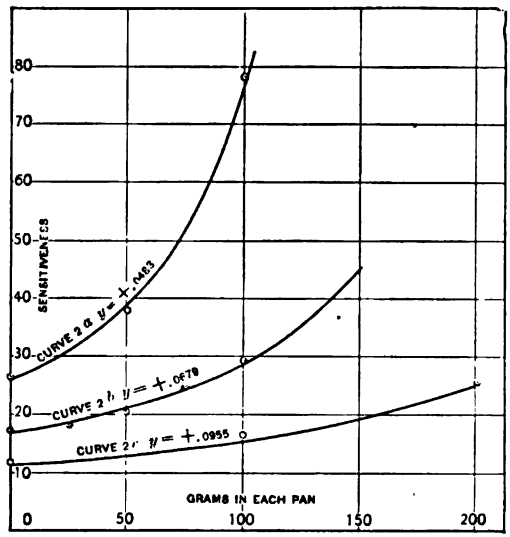

Fig. 3.

the sensitiveness varied but 5 per cent. within the limit of the balance. As this data gives .00013 cm. as the probable value of y_0', the difficulty of a closer adjustment can be appreciated. No deflections were calculated from this data.

TABLE III.

Load in Grams.	Observed Deflections.	Load in Grams.	Observed Deflections.
0	34.4	300	32.2
100	32.2	400	32.7
200	33.2		

The experiments described above made it clear that with this short, strongly trussed beam the bending of the arms is negligible with any load the knife edges should carry. In order then to check formula I. a balance having a long unbraced beam was used. It was a cheap one with steel knife edges riveted in a brass beam made by Troemner. It was found with its end knife edges below

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the central one and was very carefully bent upward until the end knife edges were slightly higher. This it was found gave the desired case of a curve which has a maximum value within the range of load.

The data in tables IV*a* and IV*b* plotted with curves IV*a* and IV*b* gives its behavior under two degrees of sensitiveness. As before the curves are plotted from formula I. using adjusted values determined

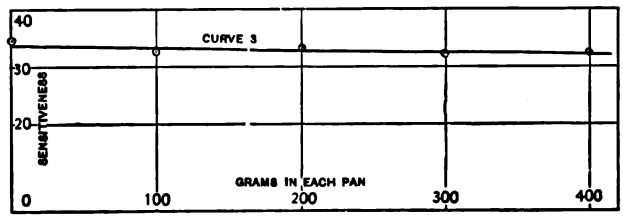

Fig. 4.

from the data in table IV*a* while the points give the observed values. Curve IV*b* is obtained by changing the value of y_0 only, the change being experimentally determined as before. The beam weighed 54.53 gr., each pan with its stirrup 43.21 gr., length of each arm 10 cm. If we collect the constants of equation I. with regard to powers of the variable W, we have

$$\frac{el}{\tan \delta} = [By_0 + 2Py_0'] + [BK + (y_0' + 2PK')]W + K'W^2.$$

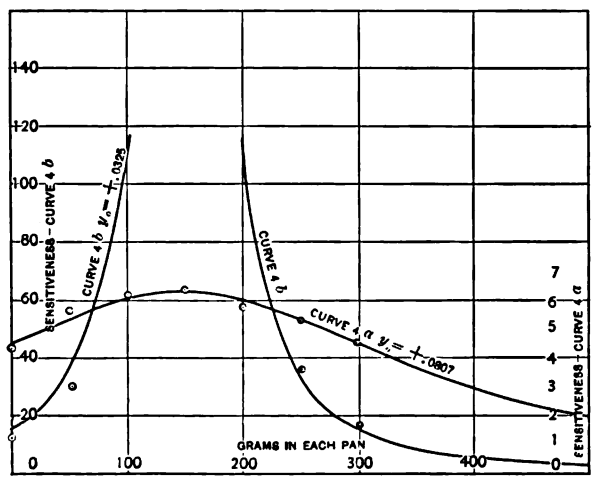

Fig. 5.

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In which y_0, y_0', K and K' are unknown quantities. These unknowns are so related that the least square adjustment will not give values for all without some further relation between them. The relation of K to K' could be calculated if the beam were of simple shape and can be estimated closely enough to give good values for the others in any case, because K is of relatively small importance in the equation. In the balance used the maximum error that would be caused by omitting K entirely is 5 per cent. The solution may also be reached by determining y_0 experimentally and then solving for the others. But since y_0 is generally large as compared to y_0', this would lead to inaccurate results. K' can be determined

TABLE IV.

Formula I. $\tan\delta = \dfrac{el}{B(y_0 + KW) + 2(P+W)(y_0' + K'W)}$. $l = 10\,cm.$ $B = 54.53$ $gr.$ $P = 43.21\,gr.$ $y_0' = -.00824.$ $K = .0000054\,cm.$ $K' = .0000238\,cm.$ $e = .01\,gr.$

IV*a*. $y_0 = +.0807\,cm.$

Load in Grams.	Deflections.		Load in Grams.	Deflections.	
	Observed.	Calculated.		Observed.	Calculated.
0	4.35	4.51	250	5.3	5.30
50	5.65	5.35	300	4.5	4.47
100	6.15	6.05	400		2.94
150	6.35	6.30	500		1.94
200	5.8	6.00			

IV*b*. $y_0 = +.0325\,cm.$

Load in Grams.	Deflections.	
	Observed.	Calculated.
0	12.60	15.65
25	——	22.60
50	29.85	36.10
75	——	62.75
100	Beyond limits of balance.	130.5
200	Beyond limits of balance.	116.0
225	——	57.0
250	36.25	32.95
300	16.55	15.05
350	——	8.65
400		5.47
500		2.82

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quite accurately by holding one end of the beam stationary as near as possible and taking observations with micrometer microscopes on the distortion produced in both ends and the middle of the beam while known loads are added to the free pan. A value of K' thus determined does not aid in solving for the other quantities but gives a good check on either of the above methods of solution.

The method followed was to estimate K'/K. For a uniform beam this ratio, derived from the equation of the elastic curve of a uniform beam, is $\frac{8}{3}$. The beam used was heavier and more rigid in the middle and after some study the value 4.4 was assumed. This gave for the adjusted values $y_0 = .0807$ cm., $y_0' = -.00824$, $K = .0000054$, $K' = .0000238$ cm. A later experimental determination of K', made as described above, gave $K' = .000024 \pm .7$ per cent.

The larger differences found between the experimental points and the theoretical curve IV*b* are easily accounted for by the fact that the balance was in a very sensitive condition and was somewhat uncertain. This uncertainty may have been due to some extent to the effect of the imperfect knife edges.

Theoretical curve IV*b* reaches infinity between 148.2 and 148.5 grams load.

WASHINGTON STATE COLLEGE,
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PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

THE CONDUCTIVITY OF THE AIR DUE TO THE SULPHATE OF QUININE.[1]

BY FANNY COOK GATES.

THE fact that the sulphate of quinine, when heated over 100° C. and allowed to cool, becomes phosphorescent and at the same time makes the surrounding air a conductor of electricity, has been the subject of a former investigation.[2] As a result of that study it was found that the ionization due to this cause has none of the characteristic properties of that due to the radiations from radioactive bodies. No satisfactory explanation of its cause was obtained although the following possible ones were suggested: (1) The conductivity of the air may be directly due to a chemical reaction in the quinine, possibly to simple hydration which is known to take place during the observed temperature change; (2) It may be caused by short ultra-violet light waves accompanying the phosphorescence, such as are known to produce ionization when they strike a negatively charged surface.

Hoping to find which of these theories might be correct, further tests were made with results as described below.

It was argued that the ultra-violet light theory would have to be rejected, if it were found that the conductivity of the air could be produced under conditions which give no trace of phosphorescence or if it could be proved directly that no ultra-violet light is present. Following these two possibilities in turn, tests were first made at low pressures.

The effect of reducing the pressure was found to greatly increase the ionization current so long as the quinine was heated in the open air before placing it in the testing vessel and exhausting. When heated electrically within the vessel at a low pressure, hardly any ionization current could be detected and it could always be entirely stopped by reëxhaustion. By keeping the quinine in this state for a half hour or more and

[1] Abstract of a paper presented at the meeting of the Physical Society held on October 28, 1905.

[2] PHYSICAL REVIEW, March, 1904.

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then allowing fresh air to enter the chamber, both the ionization and the phosphorescence resulted as with normal cooling.

Observations of the effect of cooling in damp and in dry air at atmospheric pressure showed that neither the electrical nor the optical effect could be obtained when the quinine was heated in a vessel in which P_2O_5 had been kept for several hours. Both effects were hastened when the quinine was cooled in air saturated with water vapor.

The alkaloid of quinine was sprinkled over a piece of asbestos saturated with sulphuric acid and placed between the plates of the testing vessel, but no ionization of the air could be detected during the forming of the quinine sulphate.

These observations gave such strong evidence that hydration was the cause of the phosphorescence, if not directly of the ionization, that an attempt was made to produce them without heating the quinine. Unheated quinine was kept over night in the testing vessel containing P_2O_5. The next morning, without heating the quinine, damp air was pumped into the vessel and ionization at once began and continued as before. A similar effect was produced on the phosphorescence. Thus all attempts at producing one effect without the other were unsuccessful and lead us to conclude that either the ionization is due to ultra-violet light accompanying the phosphorescence or that each is caused by hydration, independently of the other.

Direct tests for ultra-violet light, by exposing photographic plates to the phosphorescent light after it had travelled through quartz, showed no difference in the darkening of the plates from that which occurred when the quartz was replaced by glass or by air.

Tests were made with the upper plate of various materials and surfaces. Plates of zinc, brass, iron and platinum gave equal ionization currents and the ratio of the currents obtained when the lower plate was charged positively and negatively remained constant for the various plates. A surface covered with lamp-black and again with soap-film produced no change. Therefore these direct tests gave no indication of the presence of ultra-violet light.

These experiments were made in the Cavendish laboratory and I desire to express my gratitude and appreciation to Professor J. J. Thomson for his stimulating interest and advice during their progress.

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Electrolytic Mercurous Sulphate as Depolarizer for Standard Cells.[1]

By George A. Hulett.

THE problem of increasing the reproducibility of the unit of electromotive force was taken up two years ago. It had been supposed that the depolarizer was responsible for variations in the E.M.F. of standard cells and accordingly a study of mercurous sulphate, the depolarizer, was undertaken. The preliminary work showed that various samples of "chemically pure" mercurous sulphate gave variations of over a millivolt in cells in which the other materials were all the same, and it therefore seemed necessary to have a sample which would serve as a standard of reference. In order to obtain as pure a product as possible the following electrolytic method was devised.

Mercury to the depth of 2 cm. was placed in the bottom of a battery jar and over this was poured dilute sulphuric acid (1 to 6 by vol.) to a depth of 12 cm. The mercury was made the anode and a platinum wire which dipped into the acid served as cathode. As soon as the solution became saturated with mercurous sulphate, the salt began to deposit in the form of small grayish crystals. It was found necessary to provide the apparatus with a motor driven stirrer, so arranged that the L-part of the stirrer passed close to the surface of the mercury, and at a rate sufficient to prevent the solid sulphate from interfering with the anode reaction (about 150 revolutions a minute). The current density was .30 amp. per 100 cm.^{2} of mercury surface. Later results show that with lower current densities a clear white product is formed, but when this is used as depolarizer the cells have a higher and more variable E.M.F. Another important point developed by later work is that the acid used must be of greater than molecular concentration in order to avoid hydrolysis.[2]

The first mercurous sulphate used was, by chance, prepared under these essential conditions, and also precautions were taken to prevent hydrolysis by washing with a cadmium sulphate solution instead of water. This preparation was used in constructing the *D* series of four cadmium cells which were set up December 21, 1903. Materials similarly prepared were used in the *F* series of ten cells (February 15, 1904). All these cells were in perfect agreement and showed their constant value at once. On March 15, 1904, ten Clark cells were made in which the above electrolytic mercurous sulphate, washed with zinc sulphate solution, was used.

A report on these cells was made by Professor Carhart at the Wash-

[1] Abstract of a paper presented at the meeting of the Physical Society held on October 28, 1905.

[2] Hulett, Zeitsch. f. Phys. Chem., 49, 483, 1904.

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ington meeting of the American Electrochemical Society,[1] and also a paper was read at the International Electrical Congress of St. Louis, September, 1904. The cells have now been under observation for nearly two years and some idea of their constancy and temperature coefficient can be given. The agreement of the *D* and *F* series has been exceptional as variations of single cells are not over 2 parts in 100,000, but the Clark cells are not so constant as they show variations of about 5 parts in 100,000, disregarding the temporary variations due to the generation of gas at the zinc amalgam. The following table gives the values at different temperatures, taken as a mean of a large series of observations :

Temperature in Degrees.	Cadmium Cells, D and F Series.		Clark Cells, H Series.	
	Observed.	Calculated.	Observed.	Calculated.
18.0	1.01921	1.01921	1.43025	1.43021
21.1	1.01908		1.42633	
25.0	1.01893	1.018925	1.42136	1.42125
29.85	1.01870	1.01869	1.41470	1.41464

The calculated values were obtained by using the accepted temperature coefficients, and starting from the observed value at 21.1°, the temperature at which the first comparisons were made. It will be seen that the calculated values for the Clark cells are in fair agreement with the observed, while in the case of the cadmium cells the agreement is excellent. The observed values were obtained by comparison with some older cadmium cells of Professor Carhart's; these cells were made in the usual way and their value at 21.1° was taken to be 1.01936 int. volts, assuming that the Clark cell at 15° has an E.M.F. of 1.434 volts, and that the ratio of the Clark at 15° to the cadmium at 20° is 1.4067.[2] Professor Carhart kindly consented to compare these cells with his and the observations at 21.1° were made in the physical laboratory. The other observations were made by myself in the laboratory of physical chemistry at the University of Michigan. It is to be noted that the cells made with electrolytic mercurous sulphate as depolarizer are lower by .00028 volt than cells made in the usual way, and it might be added that they assumed their constant value at once, while it has been necessary to allow cells made in the old way to "age," that is they have too great an E.M.F. at first and gradually settle down to a constant value.

During the summer of 1905 it was necessary to transport the cells from Ann Arbor to Princeton, and precautions were taken to prevent jarring by packing the cells in cotton and by fastening rubber stop-

[1] Trans., vol. 5, 59, 1904.

[2] Jaeger and Lindeck, Zeitsch. f. Instk., 21, 73, 1901.

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pers to the bottom of the box. Comparisons made since arriving in Princeton show no effect of travelling, but there is evidence from other experiences which shows that jarring may alter the E.M.F. for a considerable time.

Dr. K. E. Guthe, of the Bureau of Standards, was redetermining the absolute value of the cadmium cell with a newly constructed electrodynamometer, and wished to compare his cells with mine. On the way to Princeton, a stop was made at Washington for this purpose, and two of the *F* series and some Clark cells were left with Dr. Guthe. By letter Dr. Guthe informs me that the value of the *F* series at 25° is 1.01836 absolute volts, and the cadmium cells made in the old way would be 1.01864, or .00025 volt higher than the value given by Jaeger and Lindeck (l. c.). Dr. Guthe will soon publish his results in full.

The Clark cells have a larger temperature coefficient and are not as reproducible as the cadmium cells, also there is a slow generation of gas at the zinc amalgam, which often forces the solid zinc sulphate away from the amalgam and changes the E.M.F. or breaks the contact. This difficulty may be corrected by warming this leg to 40° and allowing the gas to escape to the upper part of the cell. A more serious difficulty has arisen from the great tendency of the Clark cells to crack at the zinc side. Lord Rayleigh has attributed this to an alloying of the zinc with the platinum, causing it to expand and crack the glass. I have found that this difficulty may be easily avoided by allowing the platinum wire to extend well into the leg of the cell and covering it, except at its point, with a thin sheath of glass. This devise has now been tested for two years on my Clark cells and not one of them has cracked on the zinc side. In sealing in the platinum wire a small bead of "ruby" glass was first melted on the wire near the end, but without covering the end. A small hole was made in the leg of the cell and the bead adjusted to the hole; when the glass was quite soft the wire was pushed in to the desired position and the seal completed. In this way the wire inside the cell was covered, except at its point, with a thin sheath of glass, and the amalgam did not come in contact with that part of the wire which passed through the wall of the cell.

In many respects the Clark cell is inferior to the cadmium cell, but when both kinds are constructed, their ratio is easily and accurately determined, and this ratio gives a better criterion of the reliability of cells than can be obtained by making one kind alone. Jaeger and Lindeck (l. c.) have determined the ratio

$$\frac{\text{Clark } 15^\circ}{\text{Cadmium } 20^\circ} = 1.4067,$$

and the results so far obtained give the following values for this ratio at three temperatures:

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$$\frac{\text{Clark } 18^\circ}{\text{Cadmium } 18^\circ} = 1.4033.$$

$$\frac{\text{Clark } 21.1^\circ}{\text{Cadmium } 21.1^\circ} = 1.3997.$$

$$\frac{\text{Clark } 25^\circ}{\text{Cadmium } 25^\circ} = 1.3949.$$

When this ratio is determined over a greater range, the equation of the change of the ratio with the temperature may be given.

An attempt was made to simplify the construction of standard cells by forming the depolarizer in the cell after it had been set up. The combination — mercury | cadmium sulphate, solution | cadmium amalgam — was constructed and a current of .005 amp. passed through the cell from the mercury to the cadmium sulphate solution. The solution soon began to deposit the depolarizer at the surface of the mercury, and after about 50 mg. had been deposited the current was broken. The observations on this cell from the time of breaking the current were:

	1/2 Hour.	2 Hours.	1 Day.	3 Days.	15 Days.	30 Days.
July . . .	1.0201	1.0198	1.0196	1.0194	1.0193	1.01915

This cell never showed a constant value, the salt formed was decidedly yellow and evidently not normal mercurous sulphate. An old cell was then taken and reversed with a current of .0005 amp. for several hours, but the same yellow salt appeared, the E.M.F. was high and is still .00015 volt above its mates.

In order to obtain a depolarizer which would be in equilibrium with a cadmium sulphate solution, the system — mercury, mercurous sulphate, cadmium sulphate and solution — was rotated at 25° for two weeks. The mercuous sulphate from this system was used as depolarizer in cells I_6, I_7 and I_8. The following observations were made:

		3 Days.	7 Days.	30 Days.	45 Days.	2 Months.	3 Months.	11 Months.
I_6	1.0204	1.0200	1.0198	1.0199	1.0197	1.0196	1.0195	1.0190
I_7	1.0204	1.0200	1.0199	1.0199	1.0198	1.0196	1.0195	1.0189
I_8	1.0203	1.0200	1.0199	1.0200	1.0197	1.0197	1.0195	1.0191

These results were surprising as it was expected that the above described system had had time to come to equilibrium, and that the mercurous sulphate when used as depolarizer in cells, would show a constant value from the time the cells were put together. It will be seen from the above results that this is far from the case, and it suggests that the cathode leg of the cadmium cell is not a system in final equilibrium. There may be equilibrium at the boundary between the mercury and

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paste and another different equilibrium in the upper part of the paste. It is best to have the paste at least one centimeter deep in the cathode leg of the cell. Some cells have been made with a small amount of paste, 2 or 3 mm. deep, and were found to be in poor agreement and variable. This behavior is explicable on the above assumption and demands that attention be given to the depth of paste necessary to give constant results. At present the greatest difficulty is in making the mercurous sulphate and in preparing the paste. This difficulty might be entirely avoided if one could procure reliable paste ready for use, and this is possible since a large amount of electrolytic mercurous sulphate might be prepared, properly washed and made to a homogeneous paste. This stock paste could be tested and the value of cells made from it determined. About a year ago some paste was made, and the cells made from it at various times have agreed to the fifth decimal place. Experiments on the effects of slight impurities in the cadmium amalgam and cadmium sulphate have been made and show that these materials of sufficient purity may easily be prepared.

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NEW BOOKS.

Mathematische Einführung in die Electronentheorie. By Dr. A. H. BUCHERER. Leipzig, B. G. Teubner, 1904.

The theory of the effects due to the motion of electrically charged bodies is so full of interest, on account of the light it throws on the nature of Cathode, Becquerel and Röntgen rays, that every serious student of physics will welcome Dr. Bucherer's attempt to furnish, in a compact and convenient form, a mathematical introduction to the theory of electrons. The subject is one of considerable difficulty and at first attracted little attention, so that, till recently, only a few problems had been solved by Oliver Heaviside, J. J. Thomson and other pioneers. Now, however, the interest in the dynamics of electrons increases with each physical discovery in this field, and many mathematicians are attacking the problems and substantial progress is being made. Much of the more recent work is of a highly analytical character and an account of it would have been out of place in a book intended to serve as an introduction to the subject. Yet the reader who makes his first acquaintance with the subject from this book will not find his task always an easy one, even though the author has wisely limited his choice to those problems which admit of *comparatively* simple solutions.

The most active expounders of the theory of electrons aspire to make it give an account of the nature of ponderable matter and so to bring the whole of physical science within its domain. This is a high aim, but a theory as fundamental as that of electrons must either aim at embracing the universe or else stand self-condemned. The author, no doubt, felt bound to give a short discussion of the connexion between electrons and ponderable matter, but I shall make only this brief reference to it, as I am not competent to make any remarks upon it.

The electrical charges, whose motions are considered in this book, are either concentrated at mathematical points or are spread over spherical or ellipsoidal surfaces. For many purposes the volume of the electron may be treated as infinitesimal, but in the calculation of the energy of a moving electron or of the energy thrown off in the form of Röntgen rays, when the electron is suddenly brought to rest, it is necessary to take an electron of finite dimensions. In these cases the author follows the usual practice and assumes the electron to be a uniformly charged sphere.

After some introductory matter, Dr. Bucherer considers the steady

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rectilinear motion of a system at any speed (u) less than that of light (v), and obtains the general vector equations

$$4\pi v^2 \mathbf{D} = V\mathbf{Hu} + \mathbf{F}, \qquad \mathbf{H} = 4\pi V\mathbf{uD} + \mathbf{R}. \tag{1}$$

Here **H** and **D** are the values, in electromagnetic units, of the magnetic force and the electric displacement and $V\mathbf{Hu}$ denotes a vector product, **heavy type** denoting vectors. The quantities **F** and **R** are the mechanical forces experienced by a unit charge and a unit pole respectively, when moving at speed u along with the system. They are derivable from two *independent* potentials, ψ and φ, so that

$$\mathbf{F} = -\nabla\psi, \qquad \mathbf{R} = -\nabla\varphi. \tag{2}$$

Taking the axis of x parallel to **u**, and writing $1 - u^2/v^2 = s$, the fundamental equations

$$\operatorname{div}\mathbf{D} = \rho, \qquad \operatorname{div}\mathbf{H} = 0. \tag{3}$$

lead to the equations

$$s\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} = -4\pi v^2 s\rho, \tag{4}$$

$$s\frac{d^2\varphi}{dx^2} + \frac{d^2\varphi}{dy^2} + \frac{d^2\varphi}{dz^2} = 0. \tag{5}$$

Hence, when any value of φ satisfying (5) is known, *any* arbitrary value of ψ will furnish the solution of *some* problem, for (1) and (2) will give the values of **D** and **H**, and (3) the value of ρ at every point. The value of φ is quite independent of the distribution of ρ, so that φ does not arise from the motion of any system of electrical charges, and hence can arise only from a magnetic system. Thus φ may be put equal to zero when the motion of a purely electrical system is concerned. To get rid of φ, the author assumes (p. 29) that **H** is everywhere perpendicular to **u** and deduces that

$$\operatorname{div}\mathbf{R} = \operatorname{curl}\mathbf{R} = 0. \tag{6}$$

from which it follows that **R** is constant. In the text the author excludes a finite value for **R** on the ground that this would imply an infinite amount of magnetic energy. But this case simply corresponds to the motion of a system of charges in a *uniform* magnetic field. In a short table of errata he states that (6) implies that **R** is zero, but this is clearly an oversight. Though it is not obvious at first sight that **H** is everywhere perpendicular to **u** for any general system of charges, the property becomes evident if we start with a point-charge. For the magnetic force due to a point-charge in steady motion is in circles in planes perpendicular to **u**, and hence the magnetic force due to any number of point charges is also at right angles to **u**. In fact, when, as in this case

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$\mathbf{R} = 0$, the lines of magnetic force are the lines in which the surfaces of constant ψ are cut by planes perpendicular to $\mathbf{u}$.[1]

Throughout the book μ is taken to be unity and hence $\mathbf{H}$ is written for $\mathbf{B}$. This leads to unsymmetrical expressions like $V\mathbf{HD}$ (in place of $V\mathbf{BD}$) and thus to some loss of clearness. In this review I have, however, followed the author's notation.

The author then gives the solutions for a point charge and for a charged ellipsoid of revolution and calculates the energy of the system in the latter case. For a sphere of radius a with a charge of q *electromagnetic* units, the magnetic part of the energy comes to

$$T = \frac{q^2v^2}{8a}\left[\left(\frac{v}{u} + \frac{u}{v}\right)\log\frac{v+u}{v-u} - 2\right]$$

$$= \frac{q^2u^2}{3a}\left(1 + \frac{6}{3\cdot 5}\cdot\frac{u^2}{v^2} + \frac{9}{5\cdot 7}\cdot\frac{u^4}{v^4} + \cdots\right),$$

while the total energy is

$$\frac{q^2v^2}{2a} + \frac{q^2v^2}{2a}\left(\frac{v}{u}\log\frac{v+u}{v-u} - 2\right)$$

or

$$\frac{q^2v^2}{2a}\left(1 + \tfrac{2}{3}\cdot\frac{u^2}{v^2} + \tfrac{2}{5}\cdot\frac{u^4}{v^4} + \cdots\right).$$

The momentum of a moving electron and the idea of electromagnetic mass are next brought before the reader. Earlier in the book it is shown that the force experienced by any system of charges and due to electromagnetic action, together with the force

$$\frac{d}{dt}\int V\mathbf{DH}d\tau$$

taken throughout the volume enclosed by any surface S enclosing the system, the element of volume being $d\tau$, is equivalent to the resultant of the Maxwell stress over S. Here the differentiation with regard to the time is to be performed on the values of $\mathbf{H}$ and $\mathbf{D}$ at points *fixed in space*.

The distinction between $d\mathbf{H}/dt$ at a fixed point and $d\mathbf{H}/dt$ at a point moving with the system has been overlooked by the author in an application of this result to the case of a charged body in uniform motion when S is made to ultimately coincide with the surface of the body and when both $\mathbf{D}$ and $\mathbf{H}$ vanish at all points within the surface of the body. Since $\mathbf{D}$ and $\mathbf{H}$ vanish within the body, and since $d\mathbf{D}/dt$ and $d\mathbf{H}/dt$ also vanish *within* S, he concludes that the force on the charge carried by the

[1] Phil. Trans. Royal Society, 1896, p. 700.

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body is simply that due to the Maxwell stress acting over S. But the values of $\mathbf{D}$ and $\mathbf{H}$ at a *fixed point* change suddenly as the surface passes over the point and thus $d\mathbf{D}/dt$ and $d\mathbf{H}/dt$ have infinite values though only for an infinitely short time. The part of $(d/dt)\int V\mathbf{DH}d\tau$ corresponding to each element of the surface can be found by assuming the charge to form a layer of very small thickness.[1] If $\mathbf{D}_0$ and $\mathbf{H}_0$ denote the values of $\mathbf{D}$ and $\mathbf{H}$ just outside the layer, and if the outward normal make an angle θ with $\mathbf{u}$, then the force which has been overlooked is equal to

$$u\int V\mathbf{D}_0\mathbf{H}_0 \cos\theta\, dS.$$

In the case of a changed sphere in steady motion, it is easily seen, from symmetry, that the surface integral $u\int V\mathbf{D}_0\mathbf{H}_0 \cos\theta dS$ vanishes, when the electric and magnetic forces are entirely due to the charge on the sphere.

The force $(d/dt)\, V\mathbf{DH}$ per unit volume is perhaps most easily understood if we follow Heaviside and regard it as the sum of the two forces, $Vd\mathbf{D}/dt\cdot\mathbf{H}$ and $V\mathbf{D}\cdot d\mathbf{H}/dt$, the former arising from the action of the magnetic field on the electric current $d\mathbf{D}/dt$, and the latter from the action of the electric field upon the "magnetic current" $d\mathbf{H}/dt$. [Author's units.]

The author next supposes that the surface enclosing the system of moving charges is everywhere at an infinite distance from the system, and states that the resultant of the Maxwell stress over this surface vanishes. The resultant certainly vanishes when the motion is *steady* and the velocity is less than that of light, because E and H are then of the order r^{-2} and thus the force per unit area is of the order r^{-4}. But when the electron has acceleration, waves travel out from it at the speed of light and in these waves both E and H vary as r^{-1}, when r is very great. Thus, without special examination the resultant of the Maxwell stress over the surface cannot be equated to zero even though the surface be at an infinite distance. Two examples will perhaps make the point clearer.

When a charged sphere of radius a is brought suddenly to rest, a spherical pulse of thickness $2a$ travels outwards with the velocity of light. The electric and magnetic forces in the pulse are given by

$$E = \frac{quv \sin\theta.}{2ra\left(1 - \frac{u}{v}\cos\theta\right)}, \qquad H = \frac{E}{v},$$

where q is the charge on the sphere in electromagnetic measure, u the velocity of the sphere before it was stopped, and θ the angle between the

[1] Compare Phil. Trans. Royal Society, 1896, p. 704.

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outwa d drawn radius and the direction of u. Both **E** and **H** are perpendicular to **r** and to each other, **H** being along lines of latitude and **E** along lines of long tude. On account of the relation $E = vH$ and because **E**, **H** and **r** are mutually at right angles, the Maxwell stress is normal to the sphere and is equal to $H^2/4\pi$ per unit area. The vector $V\mathbf{DH}$ is also normal to the surface and its magnitude is $H^2/4\pi v$. If the resultant of the Maxwell stress, for any concent·ic sphere lying between the two boundaries of the pulse, be F, it is found, on integration, that when it is measured in the direction of u,

$$F = -\frac{v}{au}(U - U_0),$$

where U and U_0 are the electric energies of the sphere in steady motion and at rest. It also appears that the value of $\int V\mathbf{DH}d\tau$ for the volume contained by a sphere of radius r diminishes by the amount $2(U - U_0)/u$, during the passage of the pulse over the sphere, when measured in the direction of u, a result due to Oliver Heaviside. Since the time of passage is $2a/v$, it follows that during this time

$$\frac{d}{dt}\int V\mathbf{DH}d\tau = -\frac{v}{au^2}(U - U_0)\mathbf{u}.$$

As the sudden stopping of a charged sphere is an extreme case, it may be useful to give the value of F, the resultant of the Maxwell stress, for an electron which at the time t has a finite acceleration in the direction of u. Measuring F in the same direction as u, its value for a sphere of large radius R at the time $t + R/v$ is, in the author's units,

$$F = -\frac{1}{4\pi}\int H^2 \cos\theta dS,$$

since **H** and **E** are tangential to the sphere when R is very great.

But by Heaviside's formula,[1] in Dr. Bucherer's units,

$$H = \frac{qf\sin\theta}{vr\left(1 - \frac{u}{v}\cos\theta\right)^3}.$$

By integration the force is found to be

$$F = -q^2v^2 \cdot \frac{4f^2}{v^4} \cdot \frac{u}{5vs^4} = -Q^2 \cdot \frac{4f^2}{v^4} \cdot \frac{u}{5vs^4},$$

where Q is the charge in *electrostatic* units, and $S = 1 - u^2/v^2$. A physical conception of this result is easily obtained. For if a point, start-

[1] Nature, Nov. 6, 1902, equations (12) and (14). See Nature, Nov. 13, 1902, for corrections.

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ing from rest and moving with acceleration f acquire a velocity v while it passes over a distance l, then $v^2 = 2fl$ and thus

$$F = -\frac{Q^2}{l^2} \cdot \frac{u}{5vs^4}.$$

Hence F is $u/5vs^4$ times the force between two charges each of Q electrostatic units placed at a distance l apart.

When f is infinitesimal, F is of the second order of small quantities and may be neglected. The system is then said to be in a quasi-stationary state. It will be observed that a quasi-stationary state only exists when the acceleration of the electron has *never* reached a finite value within any finite time.

When the quasi-stationary condition prevails, the force due to electromagnetic action, experienced by the charged system is $(d/dt)\int V\mathbf{HD}d\tau$. The force which must be applied to the system by non-electromagnetic means is thus $-(d/dt)\int V\mathbf{HD}d\tau$ or $(d/dt)\int V\mathbf{DH}d\tau$ taken through all space, in addition to any force required to increase the momentum of ponderable matter. Equating this force to $d\mathbf{M}/dt$, we may call $\mathbf{M}$ the electromagnetic momentum and thus

$$\mathbf{M} = \int V\mathbf{DH}d\tau.$$

The author then shows that for a charged sphere in steady motion $M = 2T/u$. In the quasi-stationary condition, the force necessary to give the sphere the acceleration du/dt is $d\mathbf{M}/dt$. Equating this quantity to $m_t du/dt$, we have

$$m_t = \frac{dM}{du} = 2\frac{d}{du}\left(\frac{T}{u}\right),$$

and so obtain for the "longitudinal mass"

$$m_t = \frac{2q^2}{3a}\left(1 + \tfrac{6}{5}\cdot\frac{u^2}{v^2} + \tfrac{9}{7}\cdot\frac{u^4}{u^4} + \cdots\right).$$

When the sphere moves with uniform speed in a circular orbit there is acceleration at right angles to the path. When this acceleration is infinitesimal, the momentum of the system will at any instant have the component M_1 parallel to the tangent and an infinitesimal component M_2 parallel to the outward normal at each instant. If r be the radius of the path, the normal force required to change the direction of M_1 is $M_1\dot{u}/r$ or $(M_1/u)u^2/r$. Since u^2/r is the acceleration of the sphere we may write

$$m_t = \frac{M_1}{u}.$$

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In the limit M_1 becomes equal to M for the rectilinear motion and thus we have for the "transverse mass"

$$m_t = \frac{M}{u} = \frac{2T}{u^2} = \frac{2q^2}{3a}\left(1 + \frac{6}{15}\frac{u^2}{v^2} + \frac{9}{35}\cdot\frac{u^4}{v^4} + \cdots\right).$$

It may be added that the value of the infinitesimal M_2 is easily found. For if P be the tangential force required to maintain the sphere in steady motion, P changes the direction of M_2 and thus $P = M_2u/r$. But Pu, the activity of P, must be equal to $2q^2f^2/3vs^2$, the rate of loss of energy by radiation,[1] where f is the acceleration and $s = 1 - u^2/v^2$. Since $f = u^2/r$, we find

$$M_2 = \frac{2q^2u^2}{3rvs^2}.$$

When u is small, $M_1 = 2q^2u/3a$ and hence the resultant momentum is inclined to the direction of u at the very small angle au/rv.

When the normal acceleration in the circular orbit is finite we must take account not only of the radiated energy but also of the radiated momentum.

According to Mr. Heaviside,[2] if $\mathbf{N}$ be the momentum and W be the energy, which has been lost by radiation at any time, $v^2 \cdot d\mathbf{N}/dt = \mathbf{u} \cdot dW/dt$. Thus $d\mathbf{N}/dt$ is parallel to $\mathbf{u}$ whatever the direction of the acceleration. The equations now become

$$P = \frac{dN}{dt} + \frac{M_2u}{r} = \frac{u}{v^2}\cdot\frac{dW}{dt} + \frac{M_2u}{r},$$

$$Pu = \frac{dW}{dt}.$$

But $dW/dt = 2q^2f^2/3vs^2 = 2q^2u^4/3vr^2s^2$, and thus

$$M_2 = \frac{rs}{u^2}\cdot\frac{dW}{dt} = \frac{2q^2u^2}{3rvs},$$

$$P = \frac{2q^2u^3}{3vr^2s^2}.$$

The exact expression for M_2 thus differs from the approximate one by having s in the denominator instead of s^2.

The author gives the transformations by which the general equations of the field are made available for investigating the effects arising from any given motion of an electron. The electric and magnetic forces are expressed in terms of two functions $\mathbf{A}$ and φ by the equations

$$\mathbf{E} = -\frac{d\mathbf{A}}{dt} - \nabla\varphi, \qquad \mathbf{H} = \text{curl } \mathbf{A}.$$

[1] O. Heaviside, Nature, Nov. 6, 1902, equation 10.
[2] Nature, August 31, 1905.

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By means of a theorem of Beltrami the values of **A** and φ at any point P at a time t are expressed as volume integrals taken through all space. Thus

$$\mathbf{A} = \int \frac{\rho' \mathbf{u}'}{r} d\tau, \qquad \varphi = v^2 \int \frac{\rho'}{r} d\tau,$$

where r is the distance from P of the element of volume $d\tau$, ρ' is the volume density and $\mathbf{u}'$ the velocity of the electrification at $d\tau$ at the time $t - r/v$. When these formulæ for the "retarded potentials" are applied to a spherical electron with a surface charge

$$\mathbf{A} = \frac{q\mathbf{u}}{r\left(1 - \frac{u}{v}\cos\theta\right)}, \qquad \varphi = \frac{qv^2}{r\left(1 - \frac{u}{v}\cos\theta\right)},$$

where r is now the great distance of P from the center of the electron and θ is the angle between **u** and the normal drawn outwards from the sphere of radius r about the electron as center.

These formulæ are then applied to find the electric and magnetic forces at a great distance from an electron moving in any way and to calculate the energy radiated from it. This part of the book will require the reader's closest attention for the inherent difficulties are very considerable. The author would have done well if he had given a fuller discussion of the processes leading up to the values of **A** and φ. In this book and in many other books and papers on the theory of electrons, Beltrami's theorem is quoted without demonstration to the discomfort of the serious student.[1]

It is to be regretted that the author has expressed many of the most important results only in complicated vector formulæ, for very considerable skill in vector analysis is required to deduce the values of the components of **E** and **H** in ordinary coördinates from these formulæ. Vector analysis is a most valuable help in these investigations, but like many another good thing, it becomes deleterious when carried to excess.

A discussion of the Zeeman effect is given and also an account of the pulse thrown off when an electron is suddenly stopped, as in the production of Röntgen rays. By Heaviside's elegant investigation,[2] that part of the energy of a sphere which is due to its motion is deduced from the energy radiated away in the pulse. The remainder of the book is devoted to discussions on the effect of motion upon optical phenom-

[1] Sommerfeld has recently given a new and brilliant proof of the formulæ for the "retarded potential" in his paper "Simplified deduction of the field and the forces of an electron moving in any given way." Proceedings of the Koninklijke Academie van Wetenschappen te Amsterdam, Nov. 26, 1904.

[2] The Electrician, Nov. 29, 1901.

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ena, the connexion between ponderable matter and electrons and on the theory of optical dispersion.

The book thus covers a wide range of most interesting work and the author may be warmly congratulated upon having made an excellent selection of subjects.

In the second edition, which will probably be demanded, the author would have the opportunity of adding further explanations where they are needed and of correcting several misprints and small errors. He does not appear to have had any assistance in correcting for the press, and it is hardly ever wise for an author to trust entirely to his own reading of the proofs.

In its present form the book is useful and, taken as a whole, is reliable. In a revised form it might be made a most valuable text book, not too difficult for students of moderate mathematical skill, and it would then satisfy a real want.

The book is the work of one of my intimate friends. For this, as well as for other reasons, I wish it much success.

G. F. C. SEARLE.

CAVENDISH LABORATORY, CAMBRIDGE, ENGLAND.

Lehrbuch der Physik. Von O. D. CHWOLSON, Band III. Braunschweig, Vieweg, 1905. Pp. xii + 988.

The first two volumes of Professor Chwolson's treatise were translated into German by Dr. Pflaum of Riga. The translation of Volume III., which deals with the subject of heat has been admirably done by Dr. Berg of the Central Observatory in St. Petersburg.

In the introduction to chapter I., heat is described as a type of kinetic energy due to an irregular unsystematic motion of the separate particles of a body as distinguished from the motions which these particles undergo when the body moves as a whole and from regular or systematized motions such as the vibratory motions which give rise to sound waves, etc. All motions of matter which are not heat motions tend to go over into heat motion and all other forms of energy due to the motion of matter tend to transformation into heat energy. This preliminary definition of heat is followed by the consideration of temperature and the means of measuring temperature including electrical and optical pyrometry.

Chapter III. deals with the study of the expansion of solids, liquids and gases and chapter IV. with thermal capacities and specific heats.

At this point in his treatise the author introduces a variation in the traditional development of the subject in the form of a brief chapter on the transformation of various forms of energy into heat energy. The conversion of kinetic energy, due to motions of translation and rotation, of radiant energy and of the energy of the electric current and electric

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discharge are briefly outlined and the remainder of the chapter is given up to thermochemistry. Chapter VI. treats of the laws of cooling of bodies and chapter VII. to thermal conductivity.

The remainder of the volume, comprising about 500 pages, deals with hermodynamics and its applications including much new material, not found in previous general treatises on physics, concerning the liquefaction of gases and the properties of liquids and vapors at the critical point.

The volume closes with a very full and satisfactory discussion of the equilibrium of substances in contact, the phase rule and the phenomena and theory of solutions. E. L. N.

The Study of Chemical Composition. By IDA FREUND. Pp. xvi + 650. Cambridge Physical Series. The University Press, Cambridge.

This book presents in a clear and orderly manner the historical development of the theories of the constitution of matter. The attitude of the writer is that of the philosopher rather than that of the physicist or the chemist. Thus the growth of the thoughts and ideas is given the prominent place, a fact which should make the book of considerable interest to physicists and chemists.

The work begins with a chapter on the methods of modern science and the relations of theory and hypothesis. The early theories of combustion are then taken up. The phlogistic hypothesis is treated in a manner to allow of a keen appreciation of the point of view of the early workers. Lavoisier, Berthollet, Richter, Dalton, Proust, Stas and others are quoted as the author shows the development of the idea of equivalent and combining weights. Chapter VIII., with which this part of the book is concluded, deals with combining weights in a way that will be of interest to chemists.

Chapters IX. to XIX. include the development of the conceptions of the ultimate constitution of matter and the theories which in one way or another have tended to throw light upon that idea. The views of the very earliest thinkers are taken up first. Then the atomic hypothesis of Dalton, the hypotheses of Gay Lussac and Avogadro, the law of Dulong and Petit, Mitscherlich's views of the connection between crystal form and chemical composition, the periodic law, the doctrine of valency, isomerism, etc., are clearly discussed. The last chapter gives a well balanced exposition of the hypothesis of the genesis of the elements according to contemporaneous writings. Radioactivity and the modern conceptions of the complex atom are discussed quite at length.

The work is unique, in that it contains numerous and full quotations and a great deal of data taken from the original literature.

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The work will commend itself to scientists interested in the problems which are related to chemical composition and to the constitution of matter. W. C. GEER.

Atlas of Emission Spectra. HAGENBACH and KONEN. Authorized English edition by ARTHUR S. KING. London, Wm. Wesley & Son, 1905. Pp. vii + 70.

The twenty-eight photographic plates which make up this atlas afford admirably executed illustrations of the arc and spark spectra of nearly all the known chemical elements. The completeness of the collection is indeed one of its admirable features. The only elements not represented by photographs are fluorin, gallium, germanium, krypton, neon, radium, scandium, tantalum, thulium and xenon. Two plates are as a rule devoted to each spectrum, one extending through the ultra-violet and violet, the other through the blue, green, yellow and orange. The 70 pages of text accompanying the charts themselves are given up to a description of the way in which the photographs were prepared and arranged; with directions for using the various charts. There is an alphabetical list of the elements represented, an index showing the spectra given on each plate and a brief descriptive table in which the charts are taken up in order and their characteristic features are indicated.

E. L. N.

Experimentelle Untersuchung von Gases. MORRIS W. TRAVERS. Braunschweig, Vieweg & Son, 1905. Pages xii + 372.

This German translation by Dr. Estreicher of Travers' well-known volume on the study of Gases is a tribute on the part of continental physicists to an author the good qualities of whose work were immediately recognized by every English speaking physicist. The German edition has been carefully brought up to date. Dr. Estreicher has added a new chapter on the heat of vaporization of liquefied gases, in which the methods of Shearer and of Fischer and Alt are described and a comparison made with the results obtained by himself. E. L. N.

Differential Equations — a short course for engineering students. By JAMES E. BOYD. Published by the author, Ohio State University, Columbus, Ohio, 1905. Pp. vi + 54.

The range of this book is indicated by the titles of its four chapters. These are: *differential equations of the first order and degree, equations of the first order and higher degrees, differential equations of order higher than the first, linear differential equations of higher order with constant coefficients.* But little attention is given to theoretical considerations. The merit of the book consists in the large number of mechanical and

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electrical problems that are given. These ought to do much to stimulate the interest of the students for whom the author writes.

There is one serious defect that ought to be mentioned. On page 8 the author starts out to prove that an equation of the form

$$Mdx + Ndy = 0$$

is exact if

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x};$$

but, as a matter of fact, he proves the converse of this.

WILLIAM BENJAMIN FITE.

Die Elektrischen Bogenlampen. VON J. ZEIDLER. Braunschweig, Vieweg & Son. Pp. x + 143.

This little volume, which forms the sixth number of Dr. Benischke's series of handbooks of electrotechnics, treats in brief form of the arc lamp. The work is divided into four parts, the first and shortest of which contains a discussion of the electrical principles of arc lamps and arc lamp circuits. Part two, which deals with construction, is divided into three sections devoted respectively to open arcs, flame arcs, and enclosed arcs. This portion of the book is of a practical and descriptive nature and is representative essentially of arc lamp construction as it is known in the present day in Germany. The third part of the volume has to do with photometry and the application of arc lights in illumination. It is, in some respects, the most useful of all in that it deals in a practical and reasonably thorough manner with a problem which has hitherto been greatly slighted by writers on these subjects. The fourth and concluding part of Dr. Benischke's handbook deals with the installation of electric arc lamps. E. L. N.

Wireless Telegraphy, its History, Theory and Practice. By A. FREDERICK COLLINS. 8vo, pp. xi + 299. New York, McGraw Publishing Co. 1905.

In the opinion of the reviewer, the illustrations, over three hundred in number, constitute the most useful part of this book. The author has evidently devoted much time to this feature, and among the numerous diagrams and reproductions of photographs are many that could not readily be found elsewhere. Unfortunately the reproductions are often not well printed. Possibly the paper is to blame for this. Many of the photographs also, although of a kind that is not unusual in the technical press, can scarcely be looked upon as adding to the value of the book from either a scientific or technical point of view. Fig. 164, entitled

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"The Marconi System," is a good example of this class of illustrations. The half-tone represents Mr. Marconi seated at a table and thoughtfully nspecting the tape from a Morse recorder, while grouped about him are various pieces of electrical apparatus, whose nature and purpose are left to the reader's imagination. The "Fessenden System" (Fig. 205), the "Guarini Transmitter" (Fig. 172), and the "Collins Wireless Telephone" (Fig. 332), are illustrated in an equally lucid manner.

For one not already possessing some familiarity with the subject of electrical waves the book would prove entirely useless. The lack of any logical sequence in the discussion is in itself sufficiently confusing. But far more serious is the lack of clearness in the explanation of difficult points, a fault which is accentuated by carelessness in style. The book gives the impression of having been written in a hurry, after an extended but superficial examination of the literature of the subject. A few illustrations of statements follow, which are, to say the least, confusing: "Fitzgerald employed a sensitive galvanometer as a detector, the field of force created by the oscillations exerted a final influence through the galvanometer system."[1] "The monochromatic oscillator may therefore be compared to an octave of musical notes, each producing a distinct wave-length" (p. 59). "All the oscillator systems described above are known as *open circuit oscillator systems*, that is to say, they have a free period of oscillation, and therefore radiate waves with great energy, though the oscillations are quickly damped out. There is another class of oscillators termed "*closed circuit oscillator systems*, in which the period of oscillation is limited to the size of the circuit. If this has a natural period equal to that of the impressed oscillations these will be prolonged for a considerable length of time before the energy is dissipated; closed-circuit oscillators are, therefore, very feeble emitters of electric waves" (p. 61). Statements of an equally confusing character are to be found on almost every page. In reading such statements the reviewer is reminded of the quotation from Faust with which Boltzmann begins the preface to his "Vorlesungen über Maxwell's Theorie der Elektricität und des Lichtes," a quotation which would seem particularly appropriate in the case of the book now under consideration.

In the hands of one whose familiarity with the subject enables him to interpret the many obscure passages and to distinguish the inaccurate statements from those that are correct, Mr. Collins's book may in some cases be found useful. But in my opinion the field of its usefulness is very limited.

ERNEST MERRITT.

[1] This remarkable sentence (p. 148) contains all that is said regarding Fitzgerald's detector.

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THE

PHYSICAL REVIEW.

THE CAPACITY OF MICA CONDENSERS.

By Anthony Zeleny.

THE differences in the value of the capacity of the same condenser observed in determinations made at different times (with different galvanometers) have given the impression that mica condensers are not available for measurements of high precision. The manufacturers of the best condensers guarantee an accuracy of only one fourth of one per cent. and even this is not usually trusted by the purchaser. The reason for these differences is that with the method of measurement commonly employed[1] the capacity value is dependent upon the period of the galvanometer. The condenser is charged or discharged through the galvanometer and remains in circuit with it during the whole period of the first throw. The gradual liberation of the absorbed charge produces a current which flows through the coil of the galvanometer the whole period of the throw. The longer this period the greater is the amount of the absorbed charge that affects the throw, and the greater is the value obtained for the capacity of the condenser.

This difficulty can be avoided readily and the results made independent of the period of the galvanometer by opening the circuit

[1] Jenkin, Report of British Association, 1863, p. 144; 1867, p. 483. Maxwell, Electricity and Magnetism, 1881, II., p. 383. Stewart and Gee, Practical Physics, 1891, II., p. 407. Kohlrausch, Physical Measurements, 1894, p. 382. Stratton and Milliken, Exps. in Gen. Physics, 1898, p. 83. Henderson, Practical Electricity and Magnetism, 1898, p. 2,2. Carhart and Patterson, Electrical Measurements, 1900, p. 227. Schluster and Lees, Exercises in Practical Physics, 1901, p. 357. Zeleny and Erikson, Manual of Physical Measurements, 1902, p. 107. Glazebrook, Electricity and Magnetism, 1903, p. 283. Miller, Laboratory Physics, 1903, p. 356.

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after the whole measurable part of the free charge has passed and before a measurable amount of the absorbed electricity has been liberated. With this modification the capacities of good condensers can easily be determined to within 0.05 per cent. and an accuracy 0.01 per cent. is attainable. The intermittent current method[1] and the "instantaneous" charge or discharge method[2] have been described and used for measuring the capacity in terms of the free charge, and under proper conditions fulfil the above requirements. These methods, however, have not been employed generally because of the greater simplicity of the ordinary method and because no definite objection appears to have been raised to it, the dependence of the value of the capacity upon the period of the galvanometer not having been fully appreciated. The "capacity" although distinguished from "instantaneous capacity" appears to have been considered a definite quantity independent of the period of the galvanometer employed.

It is the object of this paper to point out the variations in the value of a capacity as determined by the ordinary method, to show the reasons for these variations and to describe a suitable and convenient apparatus for avoiding them and enabling the mica condenser to be used as a standard of precision.

THE DISCHARGE OF A MICA CONDENSER.

The curve of Fig. 1 shows how the quantity of electricity discharged by a good condenser varies with the time of discharge. It is seen that in the interval AB, which is usually less than .01 second, the whole measurable part of the free charge passes through the galvanometer. The absorbed charge begins to be liberated at the beginning of the discharge and continues to flow for a period greater than that of the galvanometer. In a good mica condenser,

[1] Maxwell, loc. cit., p. 384. Thomson, Phil. Trans., 1883. Glazebrook, Phil. Mag., 1884, Vol. 18, p. 98. Electrician, 25, 1890. Rosa, Phil. Mag., 1889, Vol. 28, p. 315. Thomson and Searle, Phil. Trans., 1890. Dittenberger and Gruneisen, Zs. f. Instrk., Apr., 1901, p. 112. Fleming and Clinton, Phil. Mag., 1903, Vol. 5, p. 493. Rosa and Grover, 1905, Bulletin No. 2, Bureau of Standards.

[2] Gray, Measurements in Electricity and Magnetism, 1888, I., p. 443. Glazebrook and Shaw, Practical Physics, 1893, p. 595. Tory and Pitcher, Manual of Laboratory Physics, 1901, p. 272.

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the part of the absorbed charge which is liberated in a few hundredths of a second, AC, is too small to be measurable, but in 2.5 or 5 seconds, the usual periods of the first throw of a galvanometer needle or coil, this quantity becomes considerable. If the galvanometer circuit remains closed during the whole of this time, the total quantity of electricity, DD' or EE', affecting the throw varies in galvanometers of different periods. The value of the capacity determined in this manner is, therefore, a function of the period of the galvanometer as well as of the condenser itself. It is a variable quantity not adapted for use as an accurate standard. If, however, the galvanometer circuit is opened during the interval BC the quantity of electricity discharged is definite in amount and independent of the period of the galvanometer.

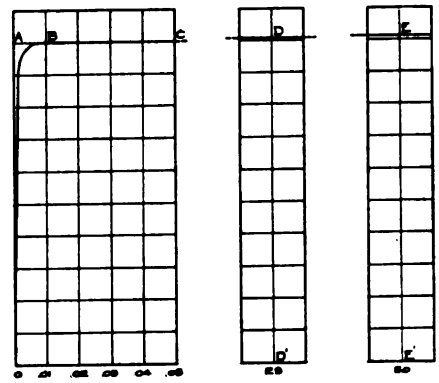

Fig. 1. Time in Seconds. Quantity Discharged.

The Discharge Key.

The special discharge key [1] adopted by the writer for determining the capacity in terms of the free charge is shown in diagram in

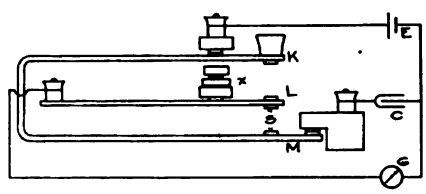

Fig. 2.

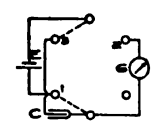

Fig. 3.

Fig. 2. In the position shown, the condenser C is being charged

[1] A well constructed (Pohl's) mercury-and-rocker commutator may be employed to accomplish the same result. The cross-bars are removed and connections made as shown in Fig. 3. The height of the mercury in the cups is adjusted so that when the rocker is turned from the charging position, shown in the figure, the cell circuit is opened first, at cup 1. The rocker then makes a contact in cup 2 before leaving cup 3, discharging the condenser during the time the two cups are in connection. The period of discharge is varied by changing the height of the mercury in cup 3.

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by means of the cell E. On depressing the key,[1] the springs K, L and M are brought into metallic connection in succession. One tap on the key (1) opens the standard cell circuit, (2) discharges the condenser through the galvanometer during the time spring K is depressing the spring L to M and (3) opens the condenser circuit when the spring L depresses the spring M. The key must be held in the last position during the whole time of the first throw.

The period during which the condenser is allowed to discharge depends on the velocity of the tap and upon the length of the space S between the springs L and M. This period is varied by maintaining an approximately uniform velocity for repeated taps while regulating the length of the space S by means of the set screw X. In the key described above this space could be made of any length up to four millimeters.

Since, for a good condenser, as shown in the curve of Fig. 1, the period BC is several times greater than the period AB, the adjustment of the key and the maintenance of a sufficiently uniform velocity of tapping give no special difficulty. The operator makes the successive taps of a nearly uniform velocity and the space S is adjusted until increasing or decreasing its length does not change the amount of the throw of the galvanometer needle or coil. This space, at the writer's velocity [2] of tapping while using a galvanometer of 127 ohms resistance and observing to .05 per cent. could be of any length from 0.5 millimeter to the full range (4 mm.) of the key. If measurements were to be made to .01 per cent. the space BC would become much shorter, necessitating a greater care in adjustment. If, in any case, it were found necessary, the key could be depressed at a more uniform rate by means of a spring, or some other device could be used to accomplish the same results with greater precision.

When the space S of the key is of the proper length, successive throws agree to within one of the estimated parts of the smallest scale division, while, when too short, the usual variations in the velocity of tapping are sufficient to affect the amount of the successive throws.

[1] The springs K, L and M are not in the same vertical plane as shown in the figure. The points of contact only are in line.

[2] Roughly estimated to be about 60 centimeters per second.

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The following tabulated throws of the galvanometer illustrate the action of the key. The discharges shown in Table I. were taken from a Leeds and Northrup Standard Condenser (one microfarad) using a very rapid velocity[1] in tapping the key. The space S regulating the period of discharge and the resistance of the galvanometer circuit were varied. The galvanometer resistance = 127 ohms. R = external resistance in the galvanometer circuit.

TABLE I.

R in Ohms.	Length of Space S in Millimeters.					
	0.2	0.5	1	2	3	4
0	19.25	19.82	19.82	19.82	19.82	19.82
	9.15	19.82	19.82	19.82	19.82	19.82
	11.05	19.82	19.82	19.82	19.82	19.82
500	4.59	12.45	17.95	18.50	19.82	19.82
	3.45	10.70	18.82	19.30	19.82	19.82
	3.88	11.63	18.23	19.70	19.80	19.82

Table II. gives the throws obtained with the above apparatus using different external resistances and a less rapid velocity[2] of tapping the key. A judgment of the approximate uniformity of successive velocities was obtained by a few up and down movements of the hand before striking the key. S = 1 millimeter.

TABLE II.

$R = 0$	$R = 500$	$R = 1{,}000$	$R = 2{,}000$
19.82	19.82	19.82	19.40
19.82	19.82	19.82	19.45
19.82	19.82	19.82	19.45

With this velocity of tapping the condenser can be used with any resistance in the galvanometer circuit up to 1,000 ohms.

FREE CHARGE AND ORDINARY CAPACITIES OF CONDENSERS OF DIFFERENT ABSORBING POWERS.

Table III. gives the observations taken with three condensers of different absorbing powers for the purpose of testing the possible

[1] Roughly estimated to be about 60 centimeters per second.

[2] Roughly estimated to be about 12 centimeters per second.

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limits of accuracy that can be attained in measuring the free charge capacities of such condensers.

(I.) = a Leeds and Northrup mica condenser (one microfarad).

(II.) = a mica condenser of large absorbing power made in the laboratory.

(III.) = a paper condenser ("2.8 microfarads").

The space S of the key was measured in terms of the number of turns made by the set screw X, Fig. 1. Each turn represents a distance of one thirty-sixth of an inch or 0.706 mm. Resistance of galvanometer = 127 ohms. Period of first throw = 2.44 seconds. Velocity of tapping key = about 60 cm. per second. Two crystal cadmium cells in series were used in charging. The readings were taken on a circular scale.

TABLE III.

Condensers.	Space S in Terms of the Number of Turns of Set Screw X.										Throws, Using the Ordinary Method.
	⅛	¼	⅜	½	¾	1	1½	2	2½	3½	
	9.60	13.11	15.70	15.71	15.71	15.71	15.71	15.71	15.71	15.71	15.83
(I.)	.10	13.54	15.71	.71	.71	.71	.71	.71	.71	.71	.83
	.25	14.10	14.60	.71	.71	.71	.71	.71	.71	.71	.83
	9.32	13.58	15.30	15.71	15.71	15.71	15.71	15.71	15.71	15.71	15.83
	11.09	12.50	15.45	15.55	15.51	15.60	15.66	15.72	15.81	15.91	18.05
(II.)	9.33	11.20	.48	.51	.56	.62	.65	.65	.70	.91	.05
	8.20	12.19	.43	.49	.56	.55	.65	.73	.75	.85	.06
	9.54	11.96	15.45	15.52	15.54	15.59	15.65	15.70	15.75	15.89	18.05
	4.54	13.26	14.70	15.00	15.45	15.82	16.33	16.92	16.92	17.81	47.24
(III.)	11.81	.63	15.82	.60	16.02	.80	.01	.90	17.50	.72	.24
	8.68	.61	14.63	.39	15.52	.84	.10	.81	16.95	.70	.26
	8.34	13.50	15.05	15.33	15.66	15.82	16.15	16.88	17.12	17.74	47.25

The observations essential for determining the point at which the whole of the free charge has passed through the galvanometer in each of the three cases are plotted in Figs. 4 and 5.

Curve I. shows that for a good mica condenser the point at which the free electricity is all discharged is definite and the residual charge produces no measurable effect for a considerable period thereafter.

Curve II. shows that for the mica condenser of high absorbing power a measurable part of the absorbed charge has affected the

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throw before the whole measurable part of the free electricity has been discharged. A close estimate of the free charge can be made from the curve. It is, however, better to consider the part of the

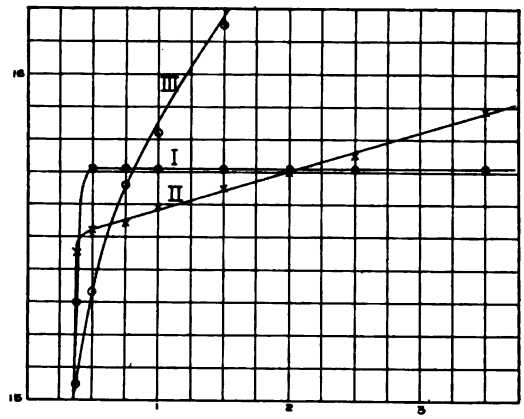

Fig. 4. Length of space S in terms of number of turns of set screw X. Throws in centimeters.

absorbed charge liberated during the interval the free electricity is discharging as a part of the free charge. With this interpretation the curve shows that the free charge capacity of this condenser can be determined to within 0.2 per cent.

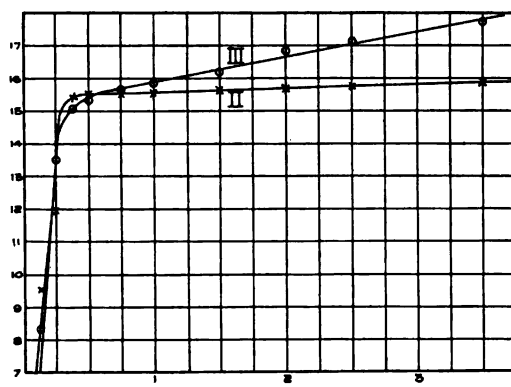

Fig. 5. Length of space S in terms of number of turns of set screw X. Throws in centimeters.

Curve III., Figs. 4 and 5, shows that in a paper condenser the free charge capacity as interpreted for condenser (II.) can be measured to within 2 per cent.

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The free charge and ordinary capacities of the three condensers as determined from Table III., with the aid of the curves of Fig. 4, are given in Table IV. The free charge capacity of condenser (I.), for the purpose of comparison, is assumed to be unity.

TABLE IV.

Condenser.	Capacities.		Difference or the Capacity Value of the Absorbed Charge Effect.	Increment to Free Charge Capacity.
	Free Charge.	Ordinary.		
(I.)	(1.0000)	1.0076	0.0076	0.76 %
(II.)	0.988	1.149	0.161	16.3
(III.)	0.96	3.008	2.05	213

The effect of the absorbed charge in condenser (II.) is seen to be more than twenty times that in condenser (I.). It has been shown that the free charge capacity of condenser (II.) can be determined to within 0.2 per cent. The free charge capacity of condenser (I.), therefore can be measured to within 0.01 per cent. An inspection of curve 1, Fig. 4, confirms this conclusion.

A further test was made on condenser (I.) by taking observations to .01 per cent. The period of the first throw of the galvanometer was increased to 9″.14 by suspending lead balls on the lower end of the coil. The observations are given in Table V.

TABLE V.

Length of Space S in Turns of Set Screw X.	
3	1
94.53 cm.	
94.52	
	94.50 cm.
	94.50
	94.51
94.53	
94.52	
94.525	94.503

This shows a difference of more than .02 per cent. for a variation of the space S by two turns of the set screw. From this in connection with an inspection of the curves of Figs. 4 and 5 it is seen that the free charge capacity of this condenser can have a well defined value only to within about .005 per cent.

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Capacities of Condensers Compared by Means of Galvanometers of Different Periods.

Table VI. shows the ordinary and the free charge capacities of three condensers as obtained with galvanometers[1] of different periods of vibration. The results were obtained by comparison with the free charge capacity of one of the condensers.

Table VI.

	Period of 1st Throw = 2″.25.		Period of 1st Throw = 4″.45.		Variation of Value of Ordinary Capacity.	Increment to Free Charge Capacity.	
	Free Charge.	Ordinary.	Free Charge.	Ordinary.		t = 2″.25.	t = 4″.45.
Leeds & Northrup (1 mcf.) (A).	(1.0000)[1]	1.0073	(1.0000)[1]	1.0114	0.41 %	0.73 %	1.14 %
Mica Condenser (poor) (B).	1.015	1.123	1.015	1.151	2.5	10.6	13.4
Paper Condenser ("1.2" mcf.)	0.46[2]	1.473[2]	0.46	1.559	5.8	220	239

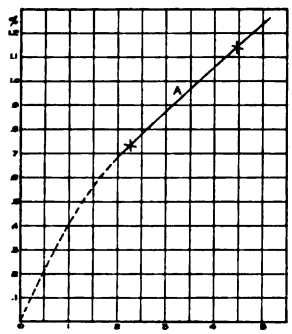

Fig. 6. Time of first throw in seconds.

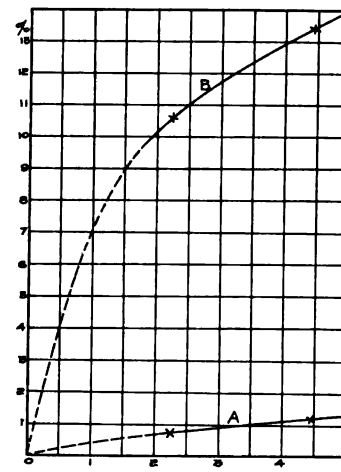

Fig. 7. Time of first throw in seconds.

Increment due to liberation of absorbed charge.

The capacities in terms of the free charge are shown to be independent of the period of the galvanometer while the ordinary "capacities" vary considerably even in the best mica condenser.

[1] The galvanometers used were both of the d'Arsonval type. The one having the shorter period has an open coil and the other a cylindrical one.

[2] Value assumed for purposes of comparison.

[3] In this case the period of the first throw of the galvanometer coil was 2″.44.

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The curves of Figs. 6 and 7 show, approximately, the increments to the free charge capacities of condensers A and B as the period of the first throw increases.

DAMPING OF THE GALVANOMETER DUE TO THE CONDENSER.

The damping correction,

$$\sqrt{\rho} = \sqrt{\frac{\theta_1}{\theta_2}},$$

was determined on open circuit and in parallel with a condenser, to test experimentally whether the condenser as used in the ordinary method had a measurable effect on the damping. An open coil d'Arsonval galvanometer was used whose coil had a resistance of 55 ohms. The capacity of the condenser was 5 microfarads.

On open circuit $\sqrt{\rho} = 1.0300 \pm 2$.

In parallel with capacity $\sqrt{\rho} = 1.0300 \pm 2$.

In the ordinary method for determining capacity, therefore, no appreciable error[1] is introduced on account of the damping due to the condenser.

RESIDUAL CHARGE VARIES AS THE E.M.F.

The amount of the first residual discharge was tested for different voltages up to 100 volts. It was found to be proportional to the electromotive force employed in charging. The capacity as determined by the ordinary method, therefore, is not influenced in value by varying the charging electromotive force.

The part of the absorbed electricity discharged during the first throw of the galvanometer coil is about one half of the first residual obtained in one minute after a discharge of the free electricity. This varies with the condenser and the period of the galvanometer.

TIME REQUIRED TO CHARGE A CONDENSER.

The difference of potential between the plates of a condenser begins to diminish immediately after the removal of the charging electromotive force on account of the gradual absorption of a part of the electric charge. The longer the time of charging the slower and smaller is the absorption after charging. A condenser must

[1] W. Einthoven, Ann. der Physik, 1905, 16, p. 20.

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therefore be charged for a sufficient length of time so that during the interval between the opening of the battery circuit and the discharge no appreciable absorption takes place.

The following observations, Table VII., were taken with the Leeds and Northrup condenser. A Crystal cadmium cell having an internal resistance of about 720 ohms was used as the charging battery. The condenser was short-circuited after each observation. It was then charged for a known period and after charging allowed to stand ten seconds before the discharge.

TABLE VII.

Time of Charging in Seconds.	Throw After Standing 10″.	Per Cent. of Charge Absorbed.
1	19.68 cm.	.75
5	19.73	.50
10	19.76	.35
15	19.79	.20
30	19.81	.10
60	19.815	.07
200	19.82	.05
300	19.83	.00
600	19.83	.00

The last two observations are the same as those obtained when the discharge was made immediately after opening the battery circuit. The condenser during the five minutes of charging had absorbed almost its maximum amount so that during the interval of ten seconds the additional part of the charge absorbed was not measurable. Fig. 8 is drawn from the data of Table VII.

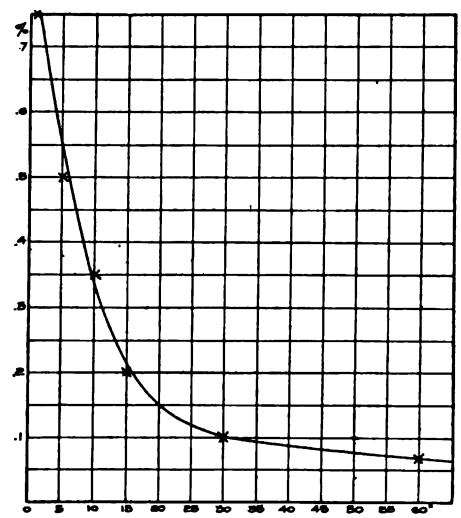

Fig. 8. Time of charging in seconds. Part of free charge absorbed.

When the observations were repeated without short-circuiting the condenser after each discharge, practically the same

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throws were obtained as before. This is due to the residual charge being nearly all liberated during the interval the condenser remains discharged. The condition of the condenser in the two cases is therefore practically the same.

When the condenser is used with the special key of Fig. 1, it is discharged almost immediately after the opening of the battery circuit. After charging the condenser one second a discharge with this key gave the maximum throw of 19.83 cm. The amount of absorption during the short interval between the opening of the cell circuit and the discharge is not measurable. When using this key, therefore, it is not necessary under ordinary conditions to give any attention to the time of charging.

Absolute Measurements.

The method here described necessitates for absolute measurements the determination of the constant of the ballistic galvanometer and the observation of a scale reading. These limit the attainable accuracy to one part in 10,000 or to .01 per cent. The intermittent current method when properly used is capable of a somewhat higher accuracy in terms of a resistance standard. For ordinary laboratory determinations, however, the method described in this paper will be found simpler and more convenient.

Comparison Measurements.

The free charge capacities can be compared to .01 per cent. by the direct deflection method. It is however preferable to use a differential method when measurements are to be made with an accuracy greater than 0.1 per cent. The writer has found the two following methods satisfactory.

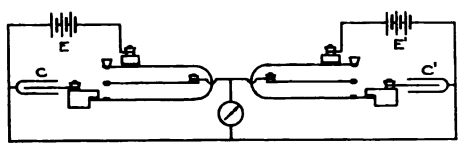

Fig. 9.

I. Each condenser is connected to a battery and a special discharge key in the usual manner except that the galvanometer used is common to both circuits and the poles of the batteries are placed in reverse order so that only the difference in the two quantities

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held by the condensers affect the galvanometer throw. The essential arrangement of the apparatus is shown in Fig. 9. The two keys are depressed by a lever (not shown in the figure) so that both condensers are connected to the galvanometer at the same instant.

(A) If the two charging electromotive forces are equal

$$q = Q - Q' = (C - C')E$$

$$C' = C - \frac{q}{E}$$

The quantity q can be made as large as desired by using the proper charging electromotive force. It is measured by comparison with a discharge from the standard condenser.

(B) If the two charging electromotive forces are only approximately equal

$$q = Q - Q' = CE - C'E'.$$

Interchanging electromotive forces,

$$q' = Q_2 - Q_3 = CE' - C'E.$$

Then

$$q + q' = (C - C')(E + E')$$

and

$$C' = C - \frac{q + q'}{E + E'}.$$

(C) When the two capacities differ greatly in value the charging electromotive forces used are such as to give approximately equal quantities of electricity in the two condensers. Then

$$q = CE - C'E'$$

and

$$C' = \frac{CE - q}{E'}.$$

In case (A) comparisons can be made to the limit of agreement of the two electromotive forces. In case (B) the quantity $(q + q')/(E + E')$ can be determined to within .01 per cent. if the condensers can withstand the electromotive forces necessary to produce a throw of sufficient magnitude. If two capacities differing

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in value by 1 per cent. have this difference measured to .01 per cent. a comparison is made to one part in a million or to .0001 per cent. This lower limit, however, has little meaning and ordinarily is difficult or impossible to be attained on account of the inequalities of the absorbed charges.

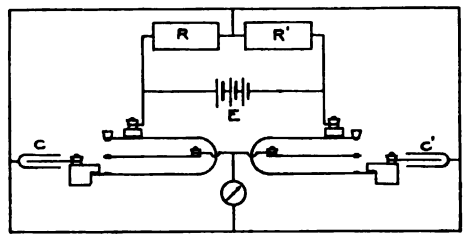

Fig. 10.

II. Another method of comparison is the well-known Thomson's method of mixtures except that the special discharge keys are substituted for the Pohl commutator ordinarily used.

The diagram of the apparatus is shown in Fig. 10. When R and R' are adjusted until no throw is obtained while depressing the keys

$$\frac{C}{C'} = \frac{R'}{R}.$$

CONCLUSION.

The capacity of a mica condenser as determined by the ordinary direct deflection method is a variable quantity and a function of the period of the galvanometer. It represents neither the unabsorbed free charge nor the total quantity of electricity held by the condenser. The capacity determined from the free charge is independent of the period of the galvanometer and dependent on the condenser only. Standards of precision must be rated, therefore, in terms of the free charge.

An interval of several hundredths of a second exists between the time of discharge of the free electricity and before the liberation of a measurable quantity of the absorbed charge. The condenser circuit must be opened during this interval. This is most conveniently accomplished by means of a special key. To avoid a loss of the free charge due to the absorption of the condenser the discharge should preferably take place immediately after charging, or the time of charging must be continued for several minutes.

The ordinary methods employed for comparing the capacities

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of condensers must also be modified so as to compare the free charges only.

The free charge capacity and the temperature coefficient[1] of a condenser being known, it becomes an instrument of precision especially useful for the accurate determination of the constants of ballistic galvanometers. For this purpose each physical laboratory should contain a condenser whose free charge capacity, including the temperature coefficient, is known to .01 per cent. The accuracy of the constants of ballistic galvanometers as determined by the condenser method employing the usual discharge key cannot be assured even to within one per cent., while with the method described in this paper it should be limited only by the accuracy with which the ballistic throws can be read.

From the considerations given in this paper and since the absorbed charge is not in the true sense a measure of a part of the capacity of a condenser the following definition appears to be more appropriate than that in present use: The capacity of a condenser is the quantity of electricity it retains *unabsorbed* while its plates are at a difference of potential of one volt.

In some cases the condenser is employed in a manner where the time is too short to allow it to become fully charged or discharged or the time is of sufficient length to cause either a part or the whole of the absorbed charge to become effective. In such cases the observed capacity value should be designated by some such term as *effective capacity*, the value being definite for that particular condition of employment only.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA.

[1] Appleyard, Phil. Mag., 1896, Vol. 46, p. 148. Cassie, Phil. Trans., 1890, Vol. 181, A, p. 1. Terry, PHYS. REV., Sept., 1905, p. 193. Rosa and Grover, *loc. cit.*, p. 185.

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PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE THIRTIETH MEETING.

THE Annual Meeting of the Physical Society was held in Fayerweather Hall, Columbia University, New York City, on Friday, December 29, and Saturday, December 30, 1905.

The Presidential Address of President Barus, on "Condensation Nuclei," was delivered on Saturday, December 30, at 11 A. M.

Friday afternoon, December 29, a joint session of the American Physical Society and the American Mathematical Society was held in Havemeyer Hall, at which a paper on the "Experimental Demonstration of Hydrodynamic Action at a Distance" was presented by Victor Bjerknes.

The following papers were presented:

1. The Electrical Production of Ozone. A. W. Ewell.
2. Some Properties of the Alpha Rays from Radium, II. E. Rutherford.
3. On the Magnetic and Electric Deviation of the Alpha Rays. E. Rutherford.
4. The Absorption of Alpha Rays in Gases and Vapors. E. P. Adams.
5. The Heating Effect produced by Roentgen Rays in Different Metals and their Relation to the Question of Changes in the Atom. H. A. Bumstead.
6. An Attempt to Explain the Cause of the Pressure Shift and the Broadening of Spectrum Lines. W. J. Humphreys.
7. Thermoelectric Heterogeneity in Certain Alloys. E. H. Hall.
8. The Relative Conductivities imparted to a Flame of Illuminating Gas by the Vapors of the Salts of the Alkali Metals. F. L. Tufts.
9. On the Specific Electrical Potentials of Metals in a Chemically Inert Atmosphere. C. B. Thwing.
10. The Optical Properties of Carbon. H. A. Clark.
11. Dispersion in Electric Double Refraction. H. L. Blackwell.
12. The Optical Properties of Extremely Thin Films. Wm. B. Cartmel.
13. The Thermodynamic Temperature Scale. Edgar Buckingham.

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14. Differential Temperature Records in Meteorological Work. C. H. McLeod and H. T. Barnes.

15. On the Velocity of Sound in Gases at Low Temperatures and the Ratio of the Specific Heats. S. R. Cook.

16. A New Determination of the E.M.F. of the Clark and Cadmium Standard Cells by means of an Absolute Electro-dynamometer. K. E. Guthe.

17. Experiments on Resonance in Wireless Telegraph Circuits. G. W. Pierce.

18. Methods of Soil Hygrometry. Edgar Buckingham.

19. Longitudinal Vibrations Analogous to those of a Violin String. H. N. Davis.

20. On the Use of the Wehmet Interrupter with the Righi Exciter for Electric Waves. A. D. Cole. (Read by title.)

21. Notes on the Possible Separation of Electric Charges by Centrifugal Accelerations. E. F. Nichols. (Read by title.)

22. The Adjustment of the d'Arsonval Galvanometer for Ballistic Work. Frank Wenner.

23. The Purpose and the Present Condition of the Mount Weather Research Observatory. W. J. Humphreys.

24. An Electrically Controlled Thermostat operable at Room Temperatures. Lyman J. Briggs.

25. On the Use of Centrifugal Force in Soil Investigations. Lyman J. Briggs.

On Saturday morning, tellers being duly appointed, the ballots received in the annual election of officers and members of the council were counted, and the following named were declared elected: *President*, Carl Barus; *Vice-President*, Edward L. Nichols; *Secretary*, Ernest Merritt; *Treasurer*, William Hallock; *Members of the Council*, R. A. Millikan and A. Trowbridge.

ERNEST MERRITT,
Secretary.

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CONDENSATION NUCLEI.[1]

BY CARL BARUS.

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INTRODUCTORY.

Steam Jet. — Before attacking the subject[2] proper, it may pay us to review the prominent methods of observing nucleation. The least pretentious of these is the transparent steam jet, which clouds up when the

[1] Presidential address before the American Physical Society, Dec. 30, 1905.

[2] References to my papers will be abbreviated as follows: B. W. B., Bulletin U. S. Weather Bureau, No. 12, 1893; S. C., Smithsonian Contributions, of the year and number specified; C. P., Carnegie Publications, No. 40, 1906.

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nuclei (caet. par.) exceed a certain number per cubic centimeter. If a millimeter steam jet actuates an air current through a 2-inch tube about 3 ft. long, sky-light guided axially through the tube becomes vividly colored in the presence of increasing nucleation, long before the opaque state sets in, and again beyond it. Loci of like color[1] may be mapped in a graph in which steam pressure and air temperature are the variables; in such a case a march at any temperature from lower to higher steam pressures, is a march from lower to rapidly higher supersaturation, and at the same time a march from purple, yellow, green and blue fields through

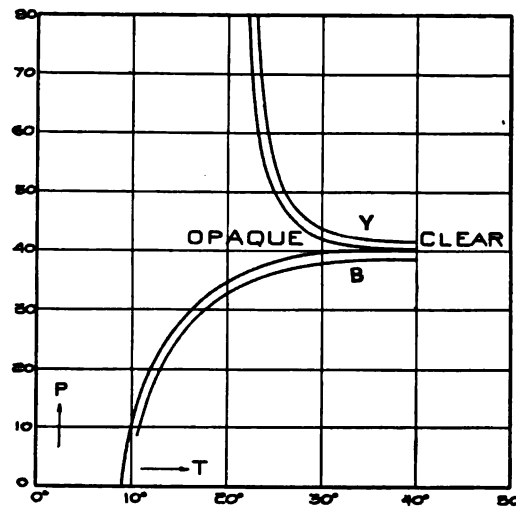

Fig. 1. Thermal topography of the steam jet, ordinates, steam pressure in lbs. per sq. inch; abscissas temperature of the inflowing air in degrees centigrade. To the right of the margin of the opaque field, the loci of blue (lower curve) and of yellow (upper curve) axial color are indicated.

opaque into brown and yellow fields. A definite degree of supersaturation is thus identified with a definite color at a given air temperature, and this constitutes the means of observation. Though the supersaturation of the steam jet may be made enormous, it does not respond usefully unless the nuclei (large or small) are present in millions per cubic cm.; for the axial colors which are evoked, require great density of nucleation to be perceptible. Ordinary atmospheric air with its tens of thousands of dust particles scarcely affects it; nor will it do so if energised by relatively weak nucleators like the X-rays or radium.[2] An order

[1] B. W. B., chaps. II. and III.

[2] These in fact usually decrease the number of efficient nuclei, as the ions are larger than the colloidal nuclei.

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of nuclei of a magnitude in question may therefore be disregarded and the air entering the steam tube treated as dust-free. This is often an advantage where excessively dense distribution of excessively fine nuclei (like those which make up a structural part of dust-free air) are to be examined. The instantaneous indication and the continuity of action of the steam jet are often further advantages. Disturbances which may be produced by sudden exhaustion and by low pressure and temperature are also absent.

Fog Chamber. — The condensation chamber in which nucleated air saturated with vapor is suddenly cooled by exhaustion, is in a measure supplementary to the steam jet, if the coronas are to be examined in all their essential features, inasmuch as it subserves the purposes of measurement best when the nucleations are fractions of a million. To be effective in the capture of very fine nuclei, its dimensions will usually have to be decreased for mechanical reasons, and the coronas may then appear only in fragments of their discs. The fog chamber of large bulk capable of entrapping widely different gradations of nuclei is thus like the steam jet, apt to be an empiric instrument; *i. e.*, the amount of cooling, the supersaturation, the water precipitated per cubic cm., cannot be computed without misgiving. In the perfected and very small form designed by C. T. R. Wilson, the data seem to warrant such a procedure; though I think there is still room to be in doubt as to what happens during the rise of temperature (heat being radiated inward from without) after complete condensation. Large coronas are characteristically fleeting and variable.

Fog Limit. — A variety of fog-chamber methods are available for specifying the nucleation as to size or number, each of which may be used empirically alone. The most accurate of these, but also the most cumbersome, is Wilson's[1] method of fog limits. There are two such points, the first being given by the supersaturation at which rain-like condensation appears (somewhat over four-fold); the second by the supersaturation required to produce cloud-like condensation (about eight-fold). Both are determined with astonishing accuracy and are of very nearly the same value (volume expansions 1.25 to 1.26 and 1.375, respectively) in the non-coercible gases. The upper limits of the orders of sizes of nuclei, corresponding to the gas in any special condition, energized or not, are measured in terms of the same datum. The actual sizes of the fog particles and the number of nuclei of the kind specified are not at once determinable by this method; but an estimate may be hazarded as to the size of the nuclei. The distribution of sizes below the maximum and their numbers are obviously beyond the scope of the method, and this has been the chief aim of the work to be summarized below.

[1] Wilson's fundamental experiments may be found in Phil. Trans. London, Vol. 189, 1897, pp. 265–307; Vol. 192, 1899, pp. 403–453; Vol. 193, 1899, pp. 289–308.

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Coronas. — The most expeditious of the relative methods for estimating numbers and sizes of fog particles is based on the measurement o coronal apertures.[1] As a method, this is naturally much less accurate than the preceding; but since the apertures vary between wide limits they are admirably suited for exploration, if the same supersaturation (*i. e.*, the same volume expansion) is used throughout. Two methods are again available, the first depending upon the direct measurement of the diameters of coronas; the second upon the reduction of the limiting size of coronas, or more specifically on the depression of the terminal asymptote corresponding in any given fog chamber to the normal case of dust-free air. The coronal method should at once suffice for the measurement of the diameters of fog particles and the nucleation would then follow from the given precipitation per cubic centimeter. Unfortunately the treatment of the diffractions even of a single small particle is a severe problem, needing (as Lommel has shown) an extensive application of Bessel's functions. It is not remarkable, therefore, that the case of indefinite assembly of particles has not been adequately stated.

Standards.[1] — In the absence of trustworthy theoretical data, the coronas must be standardized either by results obtainable or from the subsidence of fog particles whose coronas are known, or by using particles of an otherwise known diameter, or by an approximate use of diffractions under simplified conditions. With these admissions the color phenomena may be classified with a view to the determination of sizes and numbers of particles, by the aid of successive identical exhaustions into what may be called geometric sequences of coronas.

Colors.[2] — The bewildering gorgeous array of colors observed in the successive coronas for particles all of the same size, but decreasing slowly in diameter from experiment to experiment, falls naturally into three groups. In the first we may put the diffraction annuli proper, which gradually enlarge with changes of color without limit; in the second come the colors of the disc, originally white, but more and more vividly colored as the coronas are larger, and following each other in spectrum order, approximately, when the successive experiments are made with particles of decreasing smallness. On using the electric light as a source, a remnant of white disc seems, however, to remain immediately around the source. Finally the axial colors, which are identical with the colors of the steam jet, make up a third group, and they are nearly complementary in tone with the corresponding disc colors. The whole subject still needs systematic investigation. The axial colors essentially overlie or color the source of light even if this is 6 inches square, and it thus appears as if the disc colors emit the light which is axially absorbed. These phenomena are even more vivid in hydrocarbon vapors.

[1] S. C., No. 1373, chap. III.; S. C., No. 1651, chaps. III., VI., VIII.
[2] S. C., No. 1651, chap. VI.

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Apertures.[2] — The aperture of coronas is best measured to the outside of the first ring, as the contrast here between red and blue, or red and green, if ordinary light is used, is sharpest. The white and colored discs soon become vague in outline. The light should be remote from and the goniometer near the intervening fog chamber. Apertures will be found to increase as a whole, but at the same time to vary periodically with the decreasing size of fog particles. In other words, periodic variation is superimposed on regular variation, as each successive cycle of colors is run through. The cycles are definitely separable for the larger coronas; for the smaller coronas they are so crowded together as to nearly escape detection. This is rather fortunate from the practical point of view, for it admits of the measurement of nucleations below a few thousand from the apertures alone without taking into account the changes of cycle.

Subsidence. — Stokes' subsidence equation for small spherical particles is an invaluable aid for the measurement of diameters of fog particles. The use of the equation in connection with the subsidence of clays, which I made extensively[1] in 1886, did not furnish as much evidence as was anticipated; but in the case of fog particles the conditions are apparently ideal. The outstanding difficulty seems to be that the observed motions for the case of small coronas are accelerated, whereas large coronas are fleeting and change character utterly during the period of subsidence, while in general the fog line is not sharp.

Photography.[2] — Much may be learned about the distribution and size of nuclei by photographing the fog particles formed upon them, a method which has but been begun. It has been shown, however, that fog particles in a capacious fog chamber may be caught on a film of viscous oil, either for measurement under the microscope or for micro-photography. As the requirement is that of photographing drops of the order of one ten-thousandth cm. and less, it is clear that the isothermal and other conditions must be regulated to a nicety.

The endeavor to use these photographs to determine the nucleation directly, as well as to measure the diameter of fog particles runs counter to serious difficulties; but nevertheless particles of extreme fineness corresponding to the large green-blue-purple coronas and of the diameter specified have been successfully taken. It is noteworthy that whereas the photographic values for the diameters are too large and the corresponding photographic nucleations are too small, the datum computed from both for the quantity of water precipitated per cubic cm. in any given exhaustion is roughly correct.

Thus far, moreover, fog particles condensed on persistent nuclei only,

[1] Am. Journ. Sci., Vol. 37, 1889, p. 122; Bull. U. S. G. S., No. 36, 1886.

[2] S. C., No. 1651, chap. VII.

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have been photographed. Particularly in the case of the X-rays they show pronounced gradations of size compatible with the blurred coronas, and indicating the occurrence of correspondingly graded nuclei. The more important problem of photographing fog particles condensed on ions has not yet been attacked; but it presents no special difficulty beyond the cases already mastered, and it is clear that a number of important questions would be thus answerable.

Nuclei in General.

1. *Nucleation.* — The novelty and importance of the results which have accrued from investigation of the condensation of vapor precipitated by ions, has withdrawn the attention of most physicists from the functions and occurrence of the nucleus; and yet nucleation is probably the question of larger scope as it embraces not merely the physical structure of gases, but possibly even chemical affinity. It will appear, for instance, that in case of such a simple system as moist air, there is presented an apparent continuity of phases merging into, if not transcending the molecules themselves.

2. *Persistent Nuclei.* — Classified in the order of smallness, we may recognize three types of nuclei. The members of the first class are usually foreign to the gas in which they are suspended; but this is by no means necessarily so, as they may be produced in dust-free air by intense and prolonged X-radiation, or again by ultra-violet light. It is the characteristic of these nuclei that they require scarcely any supersaturation to induce condensation, that they are persistent, and that they can be separated from the gas in which they are otherwise universally present, by filtration. The term "dust" has been given to them with some justification; but this term is misleading; insofar as they enter saliently into the group of phenomena to be considered in the present address, they represent something indefinitely finer; and (with a single exceptional group) they almost always arise in an intensely ionized field. I should prefer to call them Coulier's or Aitken's nuclei, or perhaps better still, persistent nuclei.

3. *Fleeting Nuclei Ions.* — The class of nuclei next in the order of smallness are the ions. Nuclei of otherwise the same properties may however be produced, unassociated with an electrical charge, and it is suggestive that their maximum size need not be very different from that of the ions. This (as Wilson has shown) is definitely limited, requiring a supersaturation exceeding four times the normal value to induce condensation. The ions are thus, virtually at least, much below the order of size of the persistent nuclei. Moreover they are characteristically fleeting. Below the maximum dimensions they apparently show all gradations of size, and the term fleeting nuclei is not inapt. What their minimum size may be with

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increasing electrification is left open, as they merge into the nuclei of dust-free air from which they are then very difficult to distinguish. As their name implies the ions invariably carry electrical charge; but whether both entities, the fleeting nuclei and their charges, vanish at the same rate is yet to be determined. The rates are nearly the same; but on the other hand fleeting nuclei occur without charges and evanescence is very generally a function of size.

4. *Colloidal Nuclei.* — The class of nuclei next in succession is a fixed structural constituent of the gas itself. The nuclei do not carry appreciable electric charge. Their maximum size is also definitely limited as they require at least an eight-fold supersaturation to induce coronal condensation. If withdrawn from the gas they are at once restored, and are therefore essential to its chemical equilibrium. Below the maximum size they are graded, as the steam jet shows conclusively. Their minimum size is quite indefinite. It may terminate in the molecule or it may go even beyond. I prefer to regard the molecule as merely a dimension of nucleus repeated with maximum frequency because adapted to the given environment; and there is no reason why there should not be particles of ultra-molecular size permanently present within the gas to the same degree in which there are uniform gradations of particles of larger size up to the maximum. In fact with the discovery of the existence of free electrons under other conditions, such inferences are no longer disturbing.

Nuclei of the present type may be fitly called colloidal, as there is need of a distinctive name and the term colloidal nucleus is sufficiently vague.

5. *Electrons.* — Finally beyond these nuclei and in the direction of increasing smallness, the quest will be terminated by the electron itself. It would however be idle to attempt to specify what permanently resides in a gas at normal pressures beyond the colloidal nucleus, from the bearings of the present body of facts.

6. *Periods.* — If we cast an eye cursorily over the whole range of nuclei thus briefly sketched, we may note that in a march of decreasing size the alternate groups are usually ionized. The periodic occurrence of electrical quality as the dimensions of the nuclei grow continually smaller is probably fanciful; for the fleeting nuclei at least may be produced without ionization.

I shall now invite your attention to a brief review of the properties and occurrences of the successive ranges of nucleation, beginning with Aitken's or the

PERSISTENT NUCLEI.

7. *Sources. Absorption.* — The nucleus at the outset, is merely a dust particle, small enough to float in the air, but larger than the order of molecular dimensions. Such a particle precipitates condensation in an

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atmosphere sufficiently supersaturated with water or other vapor in its immediate vicinity, for the reasons long ago pointed out by Lord Kelvin (1880). Experimental support of this explanation had already been given by the work of Coulier (1875), and later in the investigation of Kiessling (1884 et seq.), of the younger Von Helmholtz (1886 to 1887), and in the atmospheric investigations of John Aitken (1880 to 1888).

Isolated nuclei however, would interest us but little; it is when they occur in thousands and in millions that they give rise to condensational phenomena of importance in the economy of nature. To produce these legions of nuclei is not impossible by mechanical means, just as we can for instance triturate a solid to a degree of impalpable fineness; but the more powerful agencies are usually chemical or at least refined physical processes. Similarly though a class of very interesting nuclei may be obtained by vigorously shaking solutions, or better by shattering the liquids in mutually impinging jets or jets impinging on a solid obstacle, nuclei are more abundantly produced by the evaporation (otherwise inappreciable) of certain concentrated hygroscopic liquids like sulphuric acid; or again by ignition, by combustion, etc. Such ignition should not be accompanied by any kinds of smoke, as the gross particles in this case are either a means of absorbing nuclei, or they capture too much of the available moisture. A clear Bunsen flame, a metal or any other solid (like glass) at a temperature approaching red heat or beyond, is a powerful nucleator. At ordinary temperatures phosphorus is subject to a peculiar kind of slow combustion, whereby nuclei are produced at 13° C. or a little below, and then produced from the smokeless body in maximum abundance. Many gaseous sulphides, the fumes of poly-sulphides, or of sulphur chloride on mixture with air, are good nucleators. Even dust-free coal gas and dust-free air, on commingling, set free nuclei probably belonging to this category.

In addition to mechanical, thermal and chemical processes, high electrical potential is a fruitful means of producing nuclei. A metal highly charged with electricity or even a glass insulator or the nodal points in the pathway of a stationary electric wave are a source of nuclei. There need be no spark, but an electric glow is in such cases probably always in evidence.

Finally certain kinds of radiation like strong ultra-violet light, or the X-rays acting with great intensity at short ranges and for a period of minutes, give rise to persistent nuclei in the dust-free air through which the radiation passes.

This means of producing them is the most interesting as they come in contact with no foreign bodies other than the walls of the vessel which holds the gas, and persistent nuclei may be produced by the X-rays within walls of water. At high exhaustions this growth of such persistent nuclei

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may be traced by the gradual depression of the terminal corona of dust-free air, as the exposure is more and more prolonged.

Air subjected to any of these sources is more or less filled with the freight of nuclei, and we have for brevity introduced the term *nucleation*, to denote the number of nuclei per cubic cm., regardless of kind or origin or other properties possessed, and considered solely with respect to their tendencies to promote condensation in a supersaturated vapor. If the nuclei left without interference outlive the period of many minutes or hours, we have called them persistent. On the other hand we have applied the term *ionization* (by contrast) to the number of electrons per cubic cm., regardless of the nuclei with which they may be associated.

An interesting property of the persistent nucleus is its absorption[1] at the walls of a vessel, or more obviously in tubes. If these are not too wide, the absorption takes place at the same rate irrespective of the diameter and substance of the tube. Since the decay of persistent nuclei is relatively negligible, the phenomena in case of phosphorus nuclei proceeds as if each nucleus of a nearly saturated region traveled in the entire absence of an electric field, with a velocity of about 3 millimeters per second; or if about $\pi/16$ of the entire number travel in a given cardinal direction, as though each nucleus had a velocity approaching 1.5 centimeters per second.

8. *Atmospheric Nucleation.* — As the sources of nuclei just referred to are such as are continually in presence in civilized communities, it is clear that the atmosphere must be loaded with nuclei, particularly so in winter, with those arising from the originally ionized products of combustion. But it would be rash to assume that the only sources of such nuclei are local or artificial, seeing that the artificially produced ionization, from its more rapid decay in comparison with the nuclei here in question, contributes nothing to atmospheric ionization. Apart from this, highly nucleated air, no matter whence the nuclei may arise, deserves attention as a medium not only of special properties and universal occurrence, but as affording opportunities for research. As the older and classic observations on kindred subjects were incidental or sporadic, it seemed that a continuous record of atmospheric nucleation taken systematically throughout a number of years would fully repay the labor of date-gathering, even on the theoretical side. From the practical side, all researches which depend on the radiation received from the sun, in meteorology or astro-physics, are in a measure furthered by a knowledge of the time and space distribution of the persistent nuclei in the atmosphere. Accordingly such a survey was begun at Providence over three years ago,[2] and is still in

[1] S. C., No. 1309, chap. III.; No. 1651, chaps. I. and II.
[2] S. C., No. 1651, chap. IX.

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progress, and during the last winter the work was supplemented by parallel observations made at Block Island.[1] Since July, moreover, contemporaneous series of data for the nucleation and ionization of the atmosphere have been recorded. Four observations were usually made daily, and in these much of detailed interest, which must be passed over here, is apparent.

In the discussion of this large body of observations, it is expedient to compute the daily means and from these to derive the average nucleation for the successive months during the period of observation. In graphs

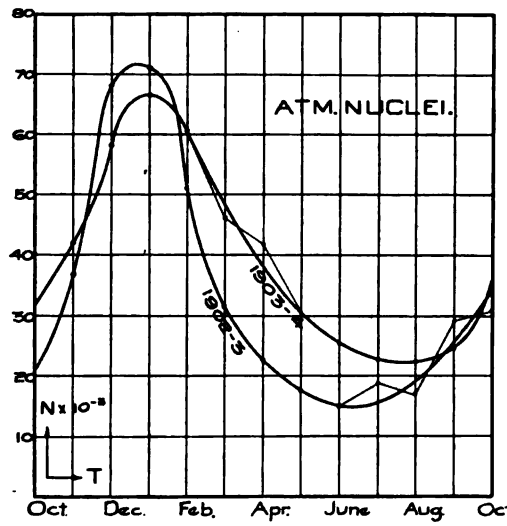

Fig. 2. Nucleation at Providence, R. I., in thousands of nuclei per cubic centimeter. The ordinates are the averages found for the successive months stated, during the years 1902–3 and 1903–4.

of this character the similarity as well as the divergence of nucleations is cogently presented. As a rule the run of incremented nucleation follows the run of decremented temperature, in a general way, throughout the year, but with more or less detail during the winter months. Again, while the nucleation curves are specifically distinct for each of the years of observation (into the details of which I cannot enter), they all have the common tendency to show sharp maxima of a value approaching one hundred thousand per cubic centimeter, at about the time of the winter sosltice, and flat minima somewhat exceeding ten thousand per cubic centimeter, near the summer solstice. It is clear from the enormous differences involved, that astronomical causes cannot be directly opera-

[1] C. P., No. 40, chaps. IV., V.

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tive, apart from the fact that the origin of the nucleation is in large measure local; but even if we agree that nucleation is powerfully depressed by rains and damp snows and possibly also (from the length of the summer day) by light pressure, the time of the winter maximum does not coincide with the period of maximum cold and of maximum combustion. A more complicated explanation is thus needed, or in any event something non-local is superimposed on what may be regarded the fairly uniform local nucleation of the winter months.

To throw light on this question, *i. e.*, to ascertain whether there may be room for a cosmical effect obscured at Providence by the dominant

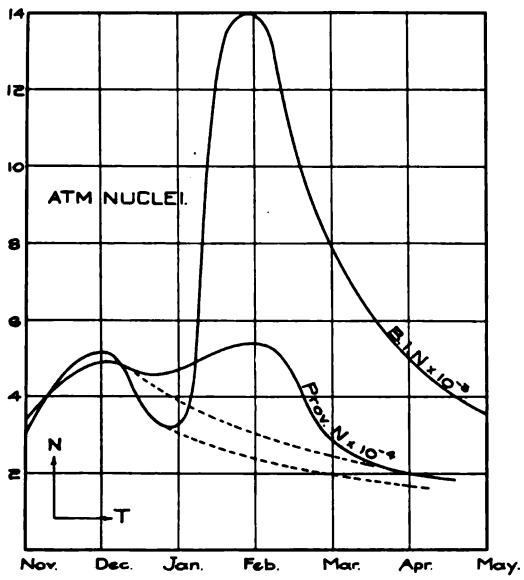

Fig. 3. Average monthly nucleations at Providence and at Block Island during the successive months stated in 1904–5. The former are given in ten thousands of nuclei per cubic centimeter, the latter in thousands of nuclei per cubic centimeter.

local distributions, observations must be made at a station where the atmosphere is less contaminated by the products of the activity of an industrial community. Block Island seemed an ideal station for the purpose, inasmuch as it would be subject to about the same meteorological changes of wind and weather as Providence, while the former is (in winter at least) nearly free from local effect. Moreover, Block Island is surrounded by a body of water, the least radius of which is nearly twenty kilometers from the center of the island, while over one half of it fronts the ocean. In any event different bodies of air would come under observation. Accordingly, measurements were taken last winter simultane-

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ously at the two stations (at Block Island by Mr. R. Pierce) by the same coronal methods.

When the curves of monthly nucleation for each place had been calculated, both suggested the results of the two preceding years, the tendency being to reach sharp maxima of nucleation in December with a rapid fall thereafter to the flat summer minimum. In both cases, however, there was a new effect in February, 1905, which, being superimposed on the high local nucleations at Providence, appears as a mere departure from the normal curves, but which juts out into striking prominence in the observations at Block Island, where the local effect is relatively negligible. Apart from quantity the fluctuations of both curves are of the same kind. Remembering that different bodies of atmospheric air arrive at the two stations, one may conclude conservatively that the coincident variations represent the diluted local effects arising on land elsewhere, but averaged by the sweep of the winds for an enormous extent of territory. It is true, too, that the minimum monthly temperature was felt in February; but neither this nor the rain distributions are adequately pronounced in their variations, to be comparable with the cotemporaneous nucleations at Block Island. It is therefore quite justifiable to depart from strict prudence in believing that at least the February maximum may represent an actual invasion of the atmosphere, on the part of some external nuclei-producing agency; and that both the nucleations *and the temperature* may have been effects of the same cause. Time alone can discriminate between these surmises.

9. *Solutional Nuclei.*[1] — If pure water is shattered into fine spray the particles must soon evaporate even in a saturated atmosphere, under the conditions of the increasing temperature which follows the sudden cooling in the fog chamber; particularly so, as with decreasing size of particle, the vapor pressure at the surface continually rises. If the liquid is a solution, however dilute, a point will be reached at which the increment of vapor pressure due to increasing curvature is equivalent to the decrement of vapor pressure due to diminishing bulk and increasing concentration. Evaporation thereafter ceases, and the particle which is now remarkably persistent in the saturated environment, may be called a water nucleus. The very frequent occurrence of rain in connection with large coronas and relatively small fog particles is referable to water nuclei.

Here probably belong the nuclei obtained from certain hygroscopic liquids like the concentrated mineral acids, all of which are remarkable nucleators and make up a class by themselves, inasmuch as the nuclei are quite without ionization. A thousand or a million or more molecules per cubic cm., may escape unobserved from such a body into the surrounding air by ordinary evaporation, in spite of the low vapor pressure.

[1] S. C., No. 1373, chap. V.

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The nuclei would be formed in a saturated atmosphere by condensation of water vapor. Sulphur and sulphide nuclei (the former most abundantly produced by the sulphur flame though emitted at a temperature almost as low as the melting point), sulphur-chloride nuclei, etc., are probably of like nature, being oxidized into sulphuric acid. They are also non-ionized.

It is not necessary, however, to make use of hypotheses; for water nuclei may be abundantly produced by merely shaking solutions,[1] or in vast numbers up to several hundred thousand per cubic cm. by high pressure jets and sprays. Wherever in experiments of the present kind, there is wheezing or bursting of small bubbles, annoying discrepancies due to water nuclei are liable to occur. The number of nuclei obtained by identically agitating solutions varies naturally both with the solvent, the solute, and the amount in solution. Identically shaking one per cent. solutions and computing the nucleation resulting from the coronas observed in each case, one may classify the results somewhat as follows: pure water 100, aqueous solutions of organic bodies 600, aqueous solutions of mineral salts 1,300, benzol solution of naphthalene or paraphine 3,000 or 5,000. It is difficult to conjecture an explanation for this demarcation of groups.

Moreover the persistence of the solutional nucleus is in direct relation to the number of nuclei produced. They are more fleeting as the solutions are more dilute; but although the coefficients increase and the nucleations decrease with increasing dilution, nevertheless in case of mineral solutions, for instance, even one ten thousandth per cent. of solute is effective.

Here I may digress by recalling that if the vapor is a hydrocarbon,[2] the fog particles must be relatively large as compared with water under like conditions. Hence the coronas are intensely brilliant and remain normal or white centered in type, even when the nuclei are present in millions per cubic cm. But for the difficulty of keeping these heavy vapors like benzol, carbon-bisulphide, etc., saturated (which may probably be overcome in a revolvable fog chamber), they would offer exceptionally good conditions for the measurement of nucleations. Again the lower order of axial colors which are faint in the steam jet now become vivid and saturated even for short columns. Finally researches on the diffusion[3] of the heavy vapors into (nucleated) air lie within the scope of the coronal method.

10. *Periodicity.*[4] — It is not possible to clean the fog chamber containing graded nuclei in a single exhaustion; even if like the ions the nuclei are fleeting. Large coronas are always evanescent. The evaporation of a fog particle does not therefore restore the original nucleus. The latter

[1] S. C., No. 1651, chap. IV.; No. 1373, chap. V.
[2] S. C., No. 1373, chap. IV.; No. 1651, chap. VI.
[3] S. C., No. 1651, chap. V.
[4] C. P., No. 40, chap. II., VI.

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is replaced by a water nucleus. This result has an important bearing on many of the phenomena of condensation. It recurs regularly in the alternation of large and small coronas (superior and inferior as they may be called) obtained in successive exhaustions under conditions of experiment which are otherwise quite identical, filtered air being introduced during the intervening interval after all fog particles have subsided. The efficient nuclei are therefore present, alternately in small and large size and in large and small numbers, respectively, the ratio being often of the order of 8 to 1. Twenty and more alterations have been recorded, but the experiment may be prolonged indefinitely. Non-energized dust-free air above the fog limit, or dust-free air energised by radium or the X-rays,

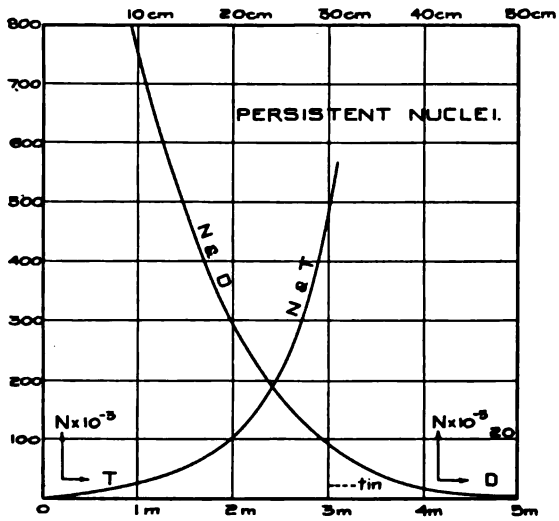

Fig. 4. Generation of persistent nuclei (ordinates, in thousands per cubic centimeter) in the lapse of minutes (abscissas): Curve N and T. Generation of persistent nuclei for the case of different distances (D in centimeters), between the X-ray bulb and the fog-chamber: Curve N and D. The dotted line "tin" shows the number produced through earthed tin plate.

have been tried and the interval between exhaustions may be varied from one to five minutes. Usually relatively high inferior coronas are followed by relatively low superior coronas and low inferior coronas are followed by high superior coronas. Coronas of mean aperture follow others of the same kind so that the periodicity ceases.

The phenomenon is not due to insufficient supersaturation, nor to the occurrence of positive and negative ions, seeing (for example) that in case of non-energised air 12,000 and 90,000 fog particles may be involved. It admits of explanation in all of its details, however, by observing that

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the smaller fog particles caught on the smaller nuclei at the end of the exhaustion evaporate into the larger fog particles and become the water nuclei of the second exhaustion. From their relatively large size, these now capture most of the moisture. In the third exhaustion the original nuclei are again available, and so on in succession. The phenomena may be beautifully exhibited by keeping the filter cock all but closed throughout. Fog particles are then continually though slowly evaporated and the coronas of successive exhaustion markedly periodic, showing efficient nucleations, in the ratio of even 15 to 1. Examples will be given in the solution of ions and colloidal nuclei.

11. *Persistent X-ray Nuclei.*[1] — These may be produced by keeping the anticathode close to the fog chamber (say 10 to 50 cm. or more), and subjecting the air to an exposure of from 2–15 minutes. Intense radiation is essential. Wooden or thin glass fog chambers are preferable. An earthed sheet of aluminum may be interposed to guard against inductive action; but this is superfluous. If produced through an earthed sheet of thin tin plate, they are naturally fewer in number. If an elongated fog chamber is used, the coronas are distorted beyond recognition and accompanied by an excessively dense fog. Many of the nuclei are very large and require scarcely any supersaturation to condense water vapor.

To describe the phenomena[2] we may suppose the X-ray bulb to be placed near one end of the fog chamber and distinguish between the near and the far halves of it. For short times of exposure the persistent nuclei are found on the near side only. The coronas are relatively small in size, roundish, decreasing in aperture to a vanishing angular radius from the near end toward the middle of the fog chamber. Beyond this the nuclei are fleeting or too small in size to respond to the given moderate exhaustion, and the far side therefore remains clear. As the time of exposure to the X-radiation is increased from one to ten minutes, the nucleations on the near side become denser and coarser and non-uniform in distribution, vertically as well as horizontally, while the efficient nuclei are found within the fog chamber at continually increasing distances from the bulb, until they eventually fill the chamber without, however, losing their characteristically graded distribution. The growth of coronas from the near to the far side as the time of exposure is increased, when seen through plate glass apparatus immediately after exhaustion, shows a curious succession of forms: they pass from round through oval, spindle-shaped, gourd-shaped (with long serpentine neck), finally to wedge-shaped diffraction patterns. Symmetry about the middle horizontal plane is maintained. Whirling rains and densely stratified

[1] C. P., No. 40, chaps. II., III., VI.
[2] C. P., No. 40, chap. I.

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fogs soon follow the condensation, so that the distribution possible for nuclei is unstable for fog particles.

These phenomena must bear on the origin of these nuclei, which are graded in size, decreasing from the near to the far side and increasing from the middle horizontal plane towards the top and bottom (in general towards the walls) of the fog chamber. In fact the forms enumerated are compatible with the diffraction patterns presumable for such gradations. Thus the case is one in which large persistent nuclei either issue from the walls of the chamber by the impact of the X-rays, or in which there is exceptionally rapid growth of nuclei in the field of ionized air adjoining those parts and due to secondary radiation. In case the number of nuclei near the middle plane of symmetry is *apparently* large because these nuclei are nearly of a size and *all* are available for consideration. Near the walls large and small nuclei are intermixed and the former capture practically all the moisture in these regions. Thus there must be many nuclei which fail of capture in the first exhaustion and for this reason the coronas on second exhaustion (without fresh nucleation and exposure to X-rays) are phenomenally large, often corresponding to one-half or to one-third of the number originally present. The large nuclei can not be solutional water nuclei, as they would not then admit of the phenomenon of secondary generation (spontaneous increase in number after radiation ceases) as will presently be explained.

12. *Decay, Exposure and Secondary Generation.*[1]—If we look at the persistent X-ray nucleus as a case in which the rate of production continually exceeds the rate of decay, there will probably be not only a growth of number in the lapse of time of exposure but also of size. In fact the nucleation generated increases at an accelerated rate into indeterminable numbers with the time of exposure for ten minutes or more, barring the invariable loss of efficiency of the X-ray bulb.

The evanescence of these nuclei through the lapse of time is characteristically slow; roughly one-half vanish in ten minutes, four-fifths in eighty minutes. The rate of decay may be estimated as about one hundred times slower than that of the ions, supposing merely for the sake of comparison, that the rates in both cases vary as the square of the nucleation. The coefficient in the terms of seconds would be about 13×10^{-9}.

The accelerated generation of persistent nucleation in the lapse of time, suggests that the nuclei themselves may contribute to this increase. This seems actually to be the case. In other words if the nucleation is observed without cutting off the radiation in one case, and if in the second case the nucleation identically produced is observed at a stated time (1–4 min.) after the radiation has ceased, the number in the latter case (anomalously enough) is an excess. In the first trials the nucleation for

[1] C. P., No. 40, chaps. III., VI.

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a lapse of four minutes without radiation is sometimes doubled. The decaying nucleus is thus *virtually* radio-active; or more simply, the large nuclei if left without interference break into a number (on the average 3) of smaller nuclei. Hence these nuclei can not be water nuclei or it would be difficult to account for their multiplication. The phenomenon vanishes when the radiation is too weak to produce persistent nuclei, therefore when either the X-ray bulb loses efficiency or is too far from the fog chamber. It is always strongest in the first exposure.

13. *Ionization.* — The nucleus as an inert excessively small body often just transcending the order of molecular dimensions, and apt to occur in immense numbers, has an interest of its own; but this interest is much enhanced, when it is found that by far the greater number of nuclei, even of the persistent type, are initially ionized, or at least carry an electric charge. The cases in which this does not occur have been instanced and are sufficiently exceptional to prove the rule. They probably admit of categorical classification. Apart from these, all nuclei produced by ignition, by high potential, by the X-rays, or even by the comminution of solution, are ionized. So marked is this quality that certain investigators (in particular the younger von Helmholtz), have endeavored to find in the ionization a sufficient cause for the condensation of supersaturated air, or at least an additional tendency to promote it. J. J. Thomson (1888) was the first, however, to adduce theoretical reasons for the condensational activity of the ions.

It is noteworthy that in all of these cases not only is ionization present, but that the ionization and the nucleation in any definite process are proportional quantities even for the case of persistent nuclei. This important result is demonstrable with phosphorous nuclei[1] by passing the charged air at different rates of flow through a tube electrical condenser into the enclosed steam tube, for the cotemperaneous measurement of the ionization and the nucleation; or again with water nuclei,[2] by conveying the comminuted water from the fog chamber where the nuclei are generated and their number ascertained through the tube condenser specified. In these cases a definite amount of both qualities is producible and may be varied under control of pleasure. Again while the nucleation within reasonable intervals of time is a fixed quantity, the number of electrons per nucleus varies with the incidentals of the experiment; but for any given adjustment the ratio is constant. Inasmuch as the ionization is subject to much more rapid decay a result of this kind would be anticipated, but detailed investigations on the rates at which the ions and the accompanying persistent nuclei are severally but simultaneously produced and decay and their relations, seem to be of the highest importance.

[1] S. C., No. 1309, chap. V.
[2] S. C., No. 1651, chap. II.

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This brings us naturally to a consideration of the fleeting nuclei or the

IONS.

14. *Characterization.*[1] — Let the X-radiation to which dust-free air is exposed be relatively weak, such as is obtained for instance from an X-ray bulb at some distance from the fog chamber, or at closer ranges by using weak radium. The density of ionization then remains below a certain critical value. The nuclei observed on condensation are small as compared with the preceding persistent class, and require a high order of supersaturation (over four-fold), approaching but always definitely below the coronal fog limit of non-energised dust-free air. Wilson showed that condensation begins at a volume expansion of 1.25, increasing thereafter with enormous rapidity. Though this is the same as the rain-like fog limit for air, the corresponding coronal phenomena lie far apart, and the impression to be gained from the charts presently to be shown is very different.

The ions are for the most purposes, instantaneously generated (within a few seconds) by the radiation, so that their number (found throughout by condensation) is practically independent of the time of the exposure, if the radiation is constant. In computing the number of ions one may assume that they are restored faster than they can be removed by exhaustion. They decay in a few seconds after radiation ceases; *i. e.*, to roughly one-half their number in two seconds, to one-fifth in twenty seconds, in the usual way. In other words, if the decay per second is as the square of the nucleation, the coefficient in terms of seconds is about 2×10^{-6}. It is therefore of about the order at which the ions decay (1.5×10^{-6}) when observed by purely electrical methods. If these rates can be shown to be quite identical in simultaneous measurements yet to be made, it would afford the strongest proof possible of the identity of the ions and fleeting nuclei in all relations. I have myself demurred from accepting this view too hastily, for the ions below the maximum dimension which in Wilson's measurements is strikingly constant, are apparently of all gradations of size, the lower limits as the intensity of ionization increases, being continuous with and eventually even overlapping the nuclei of dust-free air. They seem also at times to pass continuously into the persistent nuclei of the preceding section, where the decay of nuclei and of ions are very different things. They are abundantly produced by the gamma rays of radium, which though weak ionizers (contributing but a few per cent. of the ions) are from this point of view strong nucleators. Finally they are stable after solution, *i. e.*, after the evaporation of the fog particles precipitated upon them, while nuclei of otherwise the same properties but free from electric charge may

[1] C. P., No. 40, chaps. III., VI.

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be produced by ultra-violet light. The case thus seemed to be one in which the rate of decay soon exceeds the rate of production, so that equilibrium distributions correspond to all of the intensities of radiation by which the ions are produced. Since for a fixed value of fleeting nucleation, the rates of production and decay are the same, we may infer that if the nucleation is 10,000, 100 must be produced per cubic cm. per second; to sustain the nucleation of 100,000, 10,000 must be produced; to sustain one million, two million must be produced.

If we determine the nucleation at two pressure differences near the fog limit of the ionized air, the line so determined may be prolonged to the abscissa and the fog limit roughly ascertained. This is the coronal fog limit, and to it my remarks very largely apply. Below it there usually lies the region of rain-like condensation, which is often largely influenced by the presence of water nuclei or other influences not yet understood. In my earlier work when the intensity of radiating source was steadily increased, the increment of nucleation corresponding to a given drop if pressure varied rapidly, particularly when compared with the fog limit. The successive curves, each taken at constant ionization, are characterized by a rapid increase of slope. The course of the present address will show, however, that this must also result from a rate of exhaustion, increasingly more insufficient as the supersaturation is higher. The rate at which the nucleation increases with the pressure difference (within the limits of efficiency of the apparatus) is about the same for ions and for colloidal nuclei, though the curves lie in widely different regions of supersaturation corresponding to the different sizes of the nuclei. The slopes are preserved even in case of fog chambers of different efficiency. The reason for this is again difficult to conjecture, since the drop in pressure on exhaustion, and not the supersaturation or the volume increase is immediately in question.

15. *Persistence on Solution.*[1] — Fleeting nuclei become persistent after solution, as may be tested by evaporating the fog particles before subsidence is complete, though the rain and some fog particles will naturally drop out. Let the fog chamber be exposed to radiation for a few seconds, and thereafter exhausted below the fog limit of air, as usual. Cut off the radiation at once, rapidly measure the corona and dispel the fog by admitting filtered air. If the chamber is now left without interference for 2 to 5 or more minutes, a second exhaustion to the stated limits will show a secondary corona large relative to the primary corona. In other words, relatively many, 25–50 per cent. of the fleeting nuclei or ions caught in the first fog, have persisted; whereas without condensation, they would have practically vanished within a minute after the radiation ceased. Clearly the ions left in the wake of the evaporation specified, become solutional nuclei, in which the ion behaves as the solute. Such

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a nucleus, however small, must be large in comparison with the dissolved ion. A variety of important questions is thus suggested: Does the positive and negative electricity in a case of such solution also persist; if so (from the reduced mobility) there must be slower re-combination. Furthermore if the water nuclei holding positive ions in solution are different in size (as would be probable) from those holding negative ions in solution, there is a possibility of gravitational separation of the fog particles carrying positive and negative charges. The close relation of the whole question of solution with the occurrence of periodicity as described above, has already been instanced, and the occurrence of solution may be verified by the slightly open filter there described (§ 10).

16. *Distributiun of X-radiation.*[1] — Instead of using the X-ray bulb merely as an instrument for the production of ions, we may reverse the case and apply the wooden fog chamber from its extreme perviousness, to an investigation of nuclei-producing radiations in space. This may in a measure be done by the aid of the phosphorescent, photographic, or electrical effects, but it does not follow that the results will be identical. Using the fog chamber with moderate supersaturations the behavior is often astonishing; for when the radiation comes from any distance within a radius of 6 metres (the largest available) from the fog chamber, the fleeting nucleation produced therein is nearly the same, diminishing scarcely 5 per cent. The law of inverse squares would indicate a decrease of 10,000 to 1, within the limits of observation and the phosphorescent screen passes from intense illumination to relative darkness. Again the X-ray tube apparently emits this radiation forward as well as rearward to above 80 per cent. and 16 per cent. of the normal radiation appears even when the current is reversed. The impression gained is that of something extremely penetrating akin to the gamma rays of radium (but this impression is erroneous), and the illusion is accentuated by the fact that the radiation cannot be stopped within 50 per cent. by lead screens placed between bulb and fog chamber near the latter, even for distances of 600 cm. apart. Briefly then, this volume behaves as if the radiant field within were nearly uniform. Such a state of things is very hard to interpret.

Naturally we may explain away much of the difficulty by surrounding the fog chamber with a casket of sheet lead, one or two millimeters thick, in which case the nucleation is reduced to something like ten per cent. of its original value. More than half the radiation is thus derived from secondary sources and enters the broadsides of the fog chamber at right angles or obtusely to the primary radiation. To the eye of the uncovered chamber therefore, and for moderate supersaturations, the walls of the room are aglow with radiation, and no matter where the bulb may be placed (observationally from 6 cm. to 6 meters may intervene between

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bulb and chamber), the X-illumination derived from primary and secondary sources is about the same everywhere. Much secondary radiation must always come from the walls of the inevitable fog chamber. But all this does not explain why for moderate supersaturations the sources of secondary radiation should be unlocked about equally independent of the distance of the radiating source, within so large a space. Even if the lead case of the fog chamber is prolonged towards the bulb by a telescoping lead tube one-half of a metre long, the nucleation decreases slower than the inverse first power of the distance.

In recent experiments adapted to secure successively more rapid, and therefore higher supersaturation, the results just sketched were found to need restatement in terms of the exhaustions applied; but to do this effectively it will first be necessary to exhibit the behavior of the colloidal nuclei.

Whether or not the X-ray tube is a source of two kinds of radiation, one of which, gamma-like, is not cumulative and generates the fleeting nuclei of ions from all ranges of distance, while the other generates the persistent nuclei by cumulative action from short ranges, may be suggested for consideration. I should prefer a continuity of action of a single kind of radiation in the way already sketched.

17. *Gamma Rays.*[1] — The final subject to which I shall call your attention in connection with the ionized nuclei is a distinction between the X-rays and the gamma-rays, using in the latter instance about 10 mg. of a weak sample (10,000 ×) enclosed in a thin hermetically sealed aluminum tube. Emanation and alpha rays are thus excluded, while most of the beta rays would be absorbed in the walls of the glass or even in the wood fog chamber. Whether nucleation is markedly produced by gamma rays may then be tested, by enclosing the radium tube in a massive chamber of lead. The results are strikingly confirmatory. The nuclei are thus very largely due to this extremely penetrating radiation, inasmuch as 85 and 70 per cent. of the total number produced in the absence of the lead envelope passed through lead closed walls, one-half and one centimeter thick respectively. Secondary radiation on the outside of the fog chamber is obviously ineffective.

It does not follow, however, that nuclei are produced by the gamma rays directly. The latter more probably induce secondary radiation within the fog chamber to which the nucleation is directly due.

In comparison with the abundant nucleation after the penetration specified, the decrease of the number of nuclei observed when the radium tube is at successively greater distances from the $_{-8}$ chamber, is remarkably large. The ionized nucleation present when the radium tube touches the outside of the chamber falls off to about 17 per cent. for an

[1] C. P., No. 40, chaps. III., VI.

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external distance of 50 cm., and to about 10 per cent. for a distance of one meter. Hence, whereas the distance effect in case of the X-rays is small throughout long ranges, it is a very important consideration in case of the gamma rays of impure radium. On the other hand, the latter show a remarkable reserve of a nucleating power even after penetrating a centimeter of lead, whereas the nucleations generated by the X-rays after such penetration are negligible.

Within the fog chamber the distribution of persistent nucleation evoked by the X-rays at close range has already been sketched. When the X-rays act from long ranges the distribution of nuclei within the fog chamber is naturally quite uniform. But the same seems often to be true for radium acting at short distances. Detailed investigation, however, uncovered the complicated nature of the result obtained in this case, for the normal distance effect within is here likely to be obscured by the secondary radiation from the denser and more massive parts of the fog chamber, and by the agencies not yet well understood.

Much else might be said about ions in their condensational aspects, but time is remorseless. I must therefore hasten to consider the last of the groups in the scale of decreasing size, *i. e.*, Wilson's, or the

Colloidal Nuclei of Dust-free Air.

18. *Evidence of the Steam Jet.* — Data bearing on the graded character of colloidal nuclei in dust-free air may be variously obtained, most directly and throughout the widest range, from the behavior of the steam jet.[1] Let a millimeter jet play into a 2-inch tube, actuating a current of air in its own direction. Sky-light passing through it will then be tinged with a definite succession of colors (the axial colors of coronas), varying in a given apparatus with the steam pressure and the temperature of the inflowing air. If these two factors are kept constant, the color is fixed; but if at a given air temperature above 9° C., the pressure is increased, the succession of colors is the same as that obtained from an influx of increasingly nucleated air, at a fixed steam pressure and air temperature. This interpretation may be further verified by the addition of artificial nuclei, observing that the passage of the blues through opaque into the yellows is in the direction of increasing nucleation, or of smaller fog particles. Hence an increase of steam pressure in the absence of efficient foreign nuclei, implies an increase in the number of nuclei available for condensation, or implies an increase of the supersaturation near the jet. If, then, the steam pressure is intensified until the originally clear field, after passing a succession of colors, becomes clear again in consequence of the absence of all condensation, it follows that colloidal-air nuclei in vast numbers and of continually decreasing size must successively become

[1] Bull. U. S. W. B., No. 12, chap. III., 1895.

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available for condensation, until the fog particles are too small to be optically discernible. Each particular color corresponds to a group of nuclei characterized by their minimum size. In other words, since any color may be retained indefinitely in the field of view of the steam tube, if its temperature-pressure conditions remain unaltered, groups of nuclei to be reckoned in millions per cubic cm. must suffice for condensation, long before the molecular dimensions are approached. These groups will contain a larger number of particles as smaller particles come within the range of condensation. But even after the yellows of the first order pass into colorless fields, condensation probably still takes place on colloidal molecules, for the phenomena are still variable.

The same results may be deduced, even more cogently, perhaps, from Wilson's observation of the successive disc colors of the coronas, or most certainly from measurements of the succession of coronas in the fog chamber, presently to be examined in detail.

19. *Colloidal Nuclei Soluble.*[1] — Small as they are, the colloidal nuclei admit of solutional enlargement, as may be tested by observing the corresponding fog limits. Let the first exhaustion be made decidedly above the fog limit to obtain a corona of an appreciable size. After evaporating the fog particles by introducing filtered air into the partial vacuum, let the second exhaustion be made decidedly below the fog limit. A large corona, otherwise quite absent, will be observed. Within three minutes about 25 per cent. of the nuclei are found to persist; in ten minutes 5 per cent. are left. Without solution such nuclei are evanescent unless continually reformed.

A much more sensitive method of verifying the same fact consists in observing the depression of the limiting asymptote corresponding, in a given apparatus, to dust-free non-energized air. The more rapid the condensation the higher will be the asymptote and the more marked the lowering due to relatively few water nuclei. If the influx pipe conveying filtered air is in such a case but very slightly opened, the phenomenon of periodicity described above is strikingly in evidence in the successive exhaustions, for the reasons already given. Finally, one may bear in mind that if the act of solution were accompanied by the evolution of electric charge, otherwise inappreciable, the effect attributed here (and in the above similar cases with ions) to solution, may be regarded as evidence of electrical excitation. Specific experimental data are lacking.

Whether or not colloidal molecules are evanescent (as seems probable), they are certainly replaced faster than they can be precipitated. In computing their numbers it is assumed that they are restored to the gas at a more rapid rate than the removal by exhaustion. If different bodies of air are examined after one or more days, when all foreign nuclei must have

[1] C. P., No. 40, chaps. III. and VI.

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vanished, the coronas are a maximum for the given conditions. Hence the same conclusion is suggested.

If the filtration is slow through a wide, well-packed, cotton filter, variations of the low rates of filtration are of no consequence. There is no evidence of an addition to the nucleation from this cause. Since the nuclei are not, therefore, dragged through the filter (for which case the coronal aperture would eventually be constant, the enlargement of number being compensated by the effect of volume expansion), they must constitute an essential part of the body of air. If removed in any manner, they are at once re-instated in response to the conditions of molecular equilibrium.

The ionization of atmospheric air is undergoing constant variation. Hence it follows that the efficient nucleation of air must be correspondingly variable; for the larger ions capture relatively much of the moisture. It does not follow, however, that this variation is big enough to be ascertained by the coronal method. Nevertheless it is worth while to examine carefully filtered air for its colloidal nucleation in the lapse of time. Experiments have been in progress in Providence since May 9 of the present year, in which such nucleation is tested several times a day at the highest admissible exhaustion. It is necessary to conduct all of the operations in the same manner, preferably in duplicate apparatus; for the causes of variation are very subtle and each chamber behaves with its own coefficient. However if care be taken to have the stop-cock materially wider than the efflux pipes, so that the predominating resistance to flow shall be here, each chamber will show results which are consistent and quite trustworthy. Using the most sensitive condensation method, *i. e.*, that depending on the depression of the limiting asymptote of non-energized dust-free air, no change of the quality of scrupulously filtered atmospheric air has thus far been detected. This result is the more curious as the ions are usually present to the extent of about 1,000 to the cubic cm. Naturally these would vanish during the slow passage through the filter; but fresh ions should be reproduced within the fog chamber by the same agency which generates them without and which is not believed to be sunlight. Probably, therefore, the coronal method is as yet inadequately sensitive to cope with the variations of the small nucleation specified. At the same time the degree of constancy of the colloidal nucleation of air throughout months of observation is accentuated. After thousands of precipitations this nucleation remains both qualitatively and quantitatively the same.

20. *Natural and Induced Nucleations.*—In conclusion it may repay us to make a complete survey of the nucleations of dust-free air under any conditions. With regard to the method I may recall that the difficulties encountered were enhanced by the need of providing rapid exhaustion, in

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case of a fog chamber large enough to measure the coronas and to show the sequence of axial color. The earliest results scarcely captured the maximum of 30,000 nuclei under the extreme exhaustion corresponding to the limiting asymptote. In proportion as the apparatus was perfected, this asymptote was raised, step by step, until nucleations of 500,000 were left in the *exhausted* fog chamber. Probably the asymptote, or more accurately the terminal corona obtained in any given type of apparatus, indicates that the limit of condensing power has been reached. Between the fog limit and the terminal corona, the graph rises in a straight upward sweep; and it is remarkable that the rates at which the nucleations increase with the supersaturation or better with the drop of pressure are about the same between fog limit and asymptote, no matter whether they lie within the region of high supersaturation characteristic of the colloidal nuclei, or in a region of relatively low supersaturation characteristic of highly ionized air. Moreover they are the same in any apparatus, within the limits of its efficiency. In fact even the curve which I have endeavored to reduce to the same scale, from Wilson's disc colors for non-energised dust-free air, and which for the very small apparatus (about 4 cm. in diam.) used, naturally lies in a region of correspondingly low pressure-difference, shows a slope quite in keeping with the other curves. For an imperfect apparatus, on the other hand, the slope terminates abruptly at a lower asymptote and in a region of higher exhaustion. It will be convenient to refer to the nuclei belonging to the slope specified, as representative nuclei.

To obtain the curve for the collodial nuclei of dust free air, it is necessary to wait a week or more, until unknown internal sources of nucleation have spent themselves. Moreover the isolated observations may, with advantage, often be made hours apart; for it is with the exhaustion that the release of spurious internal nuclei occurs.

The air curve passes through the first two cycles of large coronas, terminating beyond the highest green-blue-purple, actually in the stone-blue coronas, the first of the series producible in the fog chamber by any means whatever. It corresponds with the opaques of the steam jet, beyond which, however, there exists another cycle of yellows, to my knowledge quite beyond the reach of the fog chamber. It is not probable that the medium is as yet quite optically inactive after the bluish coronas specified, but merely appears to be so in small thicknesses.

If we turn from the curve of non-energised air to the case of *weak ionization*, such as is produced by impure radium (10,000 ×) or by the X-rays from a distance of 6 meters, we may note in the first place that the coronal fog limit has enormously decreased as compared with its position in dust-free non-energised air. The nuclei are therefore throughout correspondingly larger in size. The nucleation soon rises with an ap-

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proach to the characteristic slope referred to, showing that the representative ions lie within a relatively narrow range of sizes, the curve of distribution terminating in a maximum. With increasing exhaustion the nucleation first diminishes to a minimum: Hence to all appearances the ions are now partially destroyed or else materially reduced in size at low

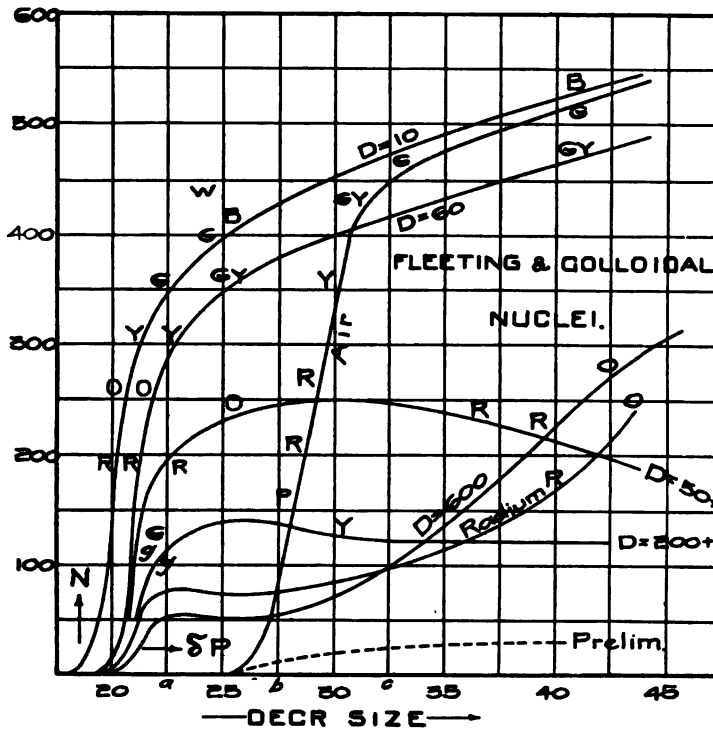

Fig. 5. Nucleation of dust-free air in thousands of nuclei per cubic centimeter, energized or not by weak radium, or by the X-rays from different distances (D in centimeters), as stated. The letters attached to the curves indicate the characteristic colors of the inner field (or its margin) of the largest coronas, the order of colors being *r o y g* (*B*). The abscissas show the sudden drop of pressure by which the supersaturation i. produced, and the nucleations apply relatively to the given apparatus only. The line marked air shows the behavior of dust-free non-energized air, terminating in the large green coronas. A line drawn from *W* to *g* roughly suggests the position of Wilson's data. In a perfect apparatus, supersaturation would increase enormously beyond *a*; the droplets would be at freezing beyond *b*. In the given apparatus efficiency probably ceases beyond *c*, when damp-air is the medium.

pressure, so as to fail of capture even in the higher exhaustions. Beyond the minimum, the final and most interesting stage of variation characteristic of weak ionization may be observed. The nucleation rapidly rises again, eventually to approach the asymptote of dust-free air.

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In explanation of this phenomenon, we may agree that further nuclei are destroyed or rendered relatively inefficient by the low pressure until there is a sufficient excess of supersaturation to actually capture the colloidal nuclei of dust-free air more and more fully in the presence of the ions (few in number and small in size) remaining. Possibly the relative number of ions and colloidal nuclei is itself a sufficient reason. Again, if the ions were agglomerated colloidal nuclei, due to the occurrence of a corpuscular kinetic pressure, it would seem plausible that for very weak ionization, the aggregates could not withstand more than low values of exhaustion.

Under *moderate ionization* such as is obtained from the X-ray bulb at a distance of 1 to 2 meters, the fog limit is definitely reduced, showing the presence of an order of larger nuclei; the asymptotes are correspondingly higher and they are reached later (*i. e.*, at higher exhaustion), indicating the presence of smaller nuclei than in the preceding cases, as well. The range of sizes within which the representative nucleations lie is definitely extended in both directions but particularly on the side of the smaller nuclei. The maximum and the minimum are flattened; though destruction of ions still occurs at low pressure.

The new feature of these curves is their failure to rise from the minimum toward the asymptote of dust-free air. It follows that the ions are now present in too large a number even relatively to their reduced sizes at high exhaustion (if this obtains) to leave an excess of supersaturation sufficient to catch the colloidal air nuclei; or from the other point of view, the kinetic ionization pressure is too strong to admit of a sufficient rupture of nuclei even at the lowest pressures applied.

In the comparison of both series of experiments, the occurrence of the intersection of the curves is noteworthy. In other words the nucleation *apparently* produced at high exhaustion by an X-ray bulb at 6 metres from the fog chamber, may be much larger than the nucleation produced from 200, 100 or even 50 cm., due (as we have supposed) to the reappearing efficiency of the colloidal nuclei in the former case. Similar complication surrounds the distance effects at other pressures: but under conditions of very moderate exhaustion, *i. e.*, below the fog limit of filtered air, the distance effect between 50 and 600 cm. remains disproportionately small.

When the ionization is relatively *intense*, as when the anticathode is from 10 to 60 cm. from the thinner sides of the glass fog chamber, the fog limit has decreased somewhat further, showing increased abundance of the larger nuclei; but the slope closely resembles the corresponding case for dust-free air. There is no maximum, but a terminal asymptote, or better a terminal corona of fixed aperture. This corona, which is here the largest obtainable in the fog chamber, is even at the highest ioniza-

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tions reached at supersaturations below the coronal fog limit for dust-free air, and long before the apparatus has ceased to function. It is impossible therefore to state whether colloidal nuclei are simultaneously present but inactive or whether their inefficiency is due to actual absence. It thus becomes a problem of great theoretical importance in its bearing on this subject to determine how the precipitated supersaturation is distributed among groups of nuclei of different sizes.

21. *Radiant Fields.* — The occurrence of a succession of groups of colloidal nuclei of (let us say for simplicity) continuously decreasing size and continuously increasing number is suggestive; for each group is essential in the given natural but otherwise unknown environment. They are at once restored if withdrawn. These conditions may be imitated or varied artificially by approaching the radium tube at different distances from the fog chamber, in which case the efficient nucleation will for weak radiation usually decrease, as the intervening distances are smaller.

Furthermore in the presence of radium the character of the phenomenon is the same, only the nuclei are throughout larger. Withdrawn by precipitation they are at once restored. They are an essential part of air in the new (radiant) environment and the nuclei are again graded.

It is natural to compare the particular nuclear status introduced in the latter case by a particular kind of radiation (gamma rays), with a former case of dust-free air in the absence of recognized radiation. In other words, if we abstract from the details of the mechanism which are unknown for the colloidal nuclei, chemical agglomeration might be considered referable to some radiant field, unknown but otherwise essentially alike in kind, to the much coarser nucleations observed on exposure to the known radiant field. The effect of radium, however distant, is virtually an increase of size of the efficient air nuclei and a decrease of their number. Hence if we were to fancy that the colloidal nucleation of air responds to its own radiant environment, this would have to be special in kind.

Recently I have made similar tentative inquiries, as to whether the ions and persistent nuclei might not be regarded as colloidal nuclei aggregated by kinetic pressure, corpuscular or undulatory. For in view of the occurrence of pronounced secondary action within the fog chamber, the radiation at any point must be considered as sufficiently the same in all directions, to be equivalent to a Lesage medium. It is then possible to account for the nucleation in any ionized field, for fleeting and persistent nuclei, for condensational differences of positive and negative ions, for fleeting nuclei otherwise identical but respectively charged and uncharged, for the destructive effect of low pressure and the counteraction in strong ionized fields, for electrical differences in the effect of ultra-violet light and of X-rays, etc., with a single straightforward hypothesis.

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While such a view may be worth a statement, it would at the outset encounter very determined opposition; and the distinctive or differentiating evidence to sustain it, is uncertain. Briefly, if we admit that with ions sufficiently large and sufficiently numerous relatively speaking, the colloidal nuclei are virtually non-existent (so far as the fog chamber is concerned), since the former capture all the available moisture, most of the phenomena of nucleation admit of interpretation, and additional hypotheses, however alluring, are not called for. Moreover so long as the representative colloidal nuclei are definitely smaller than the smaller ions, even in the strongest electrical field; in other words if what may be called the shattering action of strong fields always fails to reveal ionized nuclei as small as the representative colloidal nuclei, the special interpretation is not warranted. On any hypothesis, it nevertheless remains hard to conjecture, why an ion regarded as a loose aggregate either of molecules or of colloidal nuclei, behaves as a perfectly stable body on solution.

In conclusion, if we asked what is the most important outcome of researches of the present character, I should refer to the appearances obtained, indicating that a gas, or at least a moist gas, far from being a uniform system, behaves like an assemblage of nuclei[1] which decrease in size and increase in number as the molecular dimension is approached. Every group of nuclei is none the less a structurally essential part of the gas and (be the number of groups few or many) at once restored if withdrawn; while the molecule itself is distinguished among the many nuclei of its own kind, by the maximum frequency of occurrence.

Before closing let me acknowledge that I have dwelt all too briefly and with entirely inadequate enthusiasm on the work of my colleagues both at home and abroad: but I felt justified in taking the opportunity of this address to bring together in a connected way, the papers which from time to time I have had the honor of laying before this Society.

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[1] If for instance the colloidal nuclei were attributed to dissociations and associations due to the sudden drop of pressure (with which in fact there is a close connection), there would be no reason for the recurrence of the same phenomenon with the steam jet, where moreover high temperatures replace the low ones of the fog chamber. A mechanism of ions, dwindling at decreasing pressures in the midst of molecules, is perhaps more promising.

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The Electrical Production of Ozone.[1]

By Arthur W. Ewell.

PROFESSOR WARBURG and the writer have quite exhaustively studied the electrical production of ozone with point and plate electrodes.[2] No such study of the electrical production of ozone with an alternating current and plate electrodes separated by a dielectric has been published hitherto except for papers by Dr. A. W. Gray[3] which cover a very limited field.

During the past year the writer has conducted quite exhaustive experiments working with this type of electrodes. Current, gas velocity, form, and distance between electrodes, and dielectric were varied and for each the yield in grams per coulomb and per kilo-watt hour was determined. To briefly summarize the results: the yield per coulomb was found quite independent of the dielectric and greater the higher the gas velocity. Owing to increasing deozganization the yield increased with the current to a maximum and decreased. Narrow, bare, electrodes were most efficient. The yield per kilo-watt hour was greatest for a polar distance of a few millimeters. This type of electrodes proved far more efficient than the point and plate and than other minor types.

The Absorption of Alpha Rays in Gases and Vapors.[1]

By E. P. Adams.

THE method employed to determine the absorption of various gases and vapors for the alpha rays consists in measuring the maximum distance between a source of alpha rays and a zinc sulphide screen at which the scintillations can be seen. The source of the alpha rays is a bismuth plate rendered active by one of the radioactive substances present in the mineral carnotite — probably polonium. It is found that for any given gas or vapor the product of this maximum distance by the pressure is nearly a constant. In many cases this product increases somewhat with increasing pressure. The average value of this product is determined for a number of gases and vapors, and it is found that this product varies inversely as the sum of the square roots of the atomic weights of the atoms which make up the molecules of the substances under obser-

[1] Abstract of a paper presented at the New York meeting of the Physical Society, Dec. 29–30, 1905.

[2] Annalen der Physik., 17, 1905, p. 1.

[3] Physical Review, November, 1904, p. 347.

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vation. A similar relation was found by Bragg and Kleeman for the so-called "stopping power" of various substances for the alpha rays from radium, when measured by their ionizing effect. A number of gases and vapors, ranging in complexity from hydrogen to nickel carbonyl have been examined, with only two or three cases where the deviations seem to lie outside the limits of experimental error.

DIFFERENTIAL TEMPERATURE RECORDS IN METEOROLOGICAL WORK.[1]

BY C. H. MCLEOD AND H. T. BARNES.

IN 1897 the British Association made a grant of £50 towards an investigation of the changes in temperature due to the differences in altitude at Montreal. In the summer of 1899 an electric recording apparatus was installed in the McGill College Observatory, and arranged to read differences in temperature between the summit of Mount Royal, and the Observatory grounds. Platinum resistance thermometers were placed in the two places and connected in the first instance by No. 14 copper electric light leads. On account of the length of the run, nearly a mile, the insulation was not sufficiently good in wet weather to obtain satisfactory traces.

In the summer of 1903 a special gift from Sir Wm. Macdonald made it possible to erect a lead-covered cable, and efforts to obtain satisfactory traces were resumed with a fair amount of success. Continuous traces have been obtained for two years with but two interruptions in that time, for a few months each in the summer, and with the exception of the two stoppages, both of which were traceable to wanton interference with the cable, the cable has proved satisfactory for the work.

The thermometer on the summit of the mountain is placed on a tower 47 feet above the ground, and 800 feet above sea level, and is enclosed in a single screen cage. The thermometer in the observatory grounds is 4 feet above the surface of the soil and 180 feet above sea level, and is enclosed in a double screen cage. The difference in level of the two thermometers is seen to be 620 feet, with the Mountain thermometer in a direction approximately northwest from that on the observatory grounds. The horizontal distance is 3,300 feet and the actual length of the connecting cable is 4,100 feet including four No. 16 copper wires insulated by the ordinary telephone paper covering.

An inspection of the many traces which have been obtained shows that the temperature of the higher station is normally below that at the lower.

[1] Abstract of a paper presented at the New York meeting of the Physical Society, Dec. 29–30, 1905.

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The amount of the difference reached as much as 25 degrees Fahrenheit during the winter of 1903–4 on one or two occasions, but the average difference was from 4 to 8 degrees. The traces for the following winter did not show such great variations, the greatest being 7 degrees below the temperature of the lower station.

The most interesting feature of the records is in the manner in which an approaching change in the general temperature conditions can be observed several hours ahead on the higher thermometer. Thus the position of the trace relative to the zero, as well as whether it is rising or falling, is of the greatest importance in determining the temperature that will prevail at the lower station 10 or 12 hours later.

We have accumulated as much evidence as is possible without further experience, but so far as daily indications are concerned we have learnt to rely on the differential temperature trace and have seldom found it at fault. It is possible that the extent and duration of the difference may make it possible to form estimates for much longer periods ahead, but it will be necessary to compare a considerable number of yearly traces before definite information can be given on that point.

McGill College Observatory,
Macdonald Physics Building,
December 16, 1905.

The Relative Conductivities Imparted to a Flame of Illuminating Gas by the Vapors of the Salts of the Alkali Metals.[1]

By F. L. Tufts.

THE paper presented the results of measurements made on the relative conductivities imparted to the various types of flames of illuminating gas by the different salts of the alkali metals. The method employed was that described in a previous paper.[2] The following is a summary of the results obtained.

The supposed difference in conductivity imparted to a flame by the oxysalts and the halloid salts at high concentrations, found by Smithels, Dawson, and Wilson,[3] was shown by the experiments to be due to the different action of these salts at the platinum electrodes. When the electrode effect was eliminated by using separate electrode flames, the conductivity imparted to the connecting flame by the vapor of an equiva-

[1] Abstract of a paper presented at the New York meeting of the Physical Society, Dec. 28–30, 1905.

[2] Physical Review, Vol. XX., page 186.

[3] Phil. Trans., 193 A, p. 105.

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lent solution of KNO_3 and of KCl respectively, was found to be the same, although the concentration of the vapor in the connecting flame was so great that when the platinum electrodes were placed in this flame the current due to the KNO_3 vapor was eight times the current due to the KCl vapor, the impressed E.M.F. being two volts.

The relative conductivities imparted to a flame by equal quantities of the spray from equivalent solutions of the salts of Li, Na, and K were found to be very different for the different types of flame. When the rate of supply of gas was greatly in excess of the rate of supply of air to the burner, giving a flame rich in carbon luminosity, the relative conductivities were as follows:

$$\text{Li} = 1 \qquad \text{Na} = 6 \qquad \text{K} = 35.$$

When the rate of supply of air was much in excess of the rate of supply of gas, giving a very oxidizing B nsen flame, the relative conductivities were

$$\text{Li} = 1 \qquad \text{Na} = 6 \qquad \text{K} = 9.$$

In a flame of the first type in which the only air supplied to the burner was that blown through the atomizer, it was found that for all the salts investigated, the salt conductivity imparted to the flame was directly proportional to the rate of supply of the mixture of air and spray from the atomizer.

If we assume that a necessary condition for the formation of salt ions is the collision in the flame between oxygen and salt particles, then the rate of production of such ions, other conditions remaining the same, would vary directly as the product of the number of salt particles (n_1) into the number of air particles (n_2). Or, the rate of production of salt ions in the flame would vary directly as the square of the rate of supply of air and spray. Applying the relation which is found to hold in other cases of ionization in gases, viz.:

$$an^2 = q$$

where a is the coefficient of recombination of ions within the flame, n the number of free salt ions in the flame, and q the rate of formation of such ions. Since q is proportional to $n_1 n_2$ we may write,

$$an^2 = n_1 n_2,$$

or

$$n = N/\sqrt{a},$$

where N is proportional to the rate of supply of air and spray to the flame. Since the salt conductivity of the flame is directly proportional to the number of free salt ions (n), it follows that it would be directly

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proportional to the rate of supply of air and spray (N). The measurements showed this to be the case.

The above deduction would only hold strictly true in case there were no recombination between salt ions and flame ions within the flame. The fact that one gets such consistent results by treating the flame conductivity and the salt conductivity as simple additive quantities would indicate that within the flame there is no recombination between the two kinds of ions.

The Optical Properties of Exceedingly Thin Films.[1]

By Wm. B. Cartmel.

THIS work which was mostly done during the summer of 1905 was undertaken to determine the behavior with regard to light of films whose thickness was very much less than a wave-length. I experimented upon five fuchsine films varying in thickness from about a wave-length to $\frac{1}{800}$ of a wave-length. Wishing to determine the thickness by other than optical means I dissolved films whose area was known, in a definite quantity of alcohol and knowing the specific gravity of solid fuchsine, I could determine from the concentration the amount of fuchsine in solution and hence the thickness of the film.

The th nnest films had scarcely a measurable absorption for any color, but the amount of light reflected could be measured with a considerable degree of precision. The changes of phase produced by the thick films I have already measured, and I am engaged in measuring this from the thinner films.

The paper contains also a theoretical discussion of the reflection and refraction by thin films.

On the Velocity of Sound in Gases at Low Temperatures and the Ratio of the Specific Heats.[1]

By S. R. Cook.

THE purpose of the experiments set forth in this paper was primarily to determine the velocity of sound in air and oxygen at temperatures at which these gases would be in their vapor condition. Greely had made a series of experiments on the velocity of sound at temperature as low as $-79°$ F. Within the limit of accuracy of his experiments,

[1] Abstract of a paper presented at the New York meeting of the Physical Society, Dec. 29–30, 1905.

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Greely found that the velocity of sound decreased 60.3 cm. per degree centigrade and that the ratio of the specific heats was constant.

Withkowski, Stevens, Kalahne and Lonncke, all have made observations or deductions on the variation of the specific heats, with temperature and pressure, and have come to different conclusions, when the variation was carried far enough. The paper deals only with the variation of the ratio of the specific heats with the variation of temperature.

The velocity of sound was measured, at the temperature of liquid air, by the usual Kundt method. The comparison sound tube was introduced into a Dewar bulb, filled with liquid air.

The apparatus was so arranged that the direct ratio of the wave-lengths could be measured, and the ratio of the specific heat computed from the formula,

$$\nu = \nu' \rho \left(\frac{\lambda}{\lambda'}\right),$$

where ν and ν' and λ and λ' are the ratios of the specific heats, and the wave-lengths of sound, respectively, in the gas at two different temperatures; and ρ is the relative density of the gas at the respective temperatures.

A series of measurements were made on air at the temperature of liquid air, and it was shown that the velocity decreased more than could be accounted for by the relative variation in the density, in accordance with the Boyle-Gay Lussac-Avagadro law.

Oxygen, at the temperature of liquid air, was below its critical temperature, at atmospheric pressure, and the measurements were made at reduced pressure. The same tendency was observed in oxygen as in air.

When the ratio of the specific heats was determined from the simple formula above, the measurements showed, that, when these gases were in their vapor state, the ratio of the specific heats decreased slightly. The ratio of the internal to the external energy of the molecule was also computed from the data.

The simple formula for connecting the ratio of the specific heat with the ratio of energies is,

$$\beta + 1 = \frac{2}{3} \frac{1}{\nu - 1},$$

where β is the ratio of the internal to the external energies of the molecules. As ν decreased at low temperature, β increased correspondingly. Formulæ were deduced by the application of the characteristic equation of Clausius and also of Van der Waals; and applied to the computation of β. The corrections were very small, much less in fact than the probable error in the determination of β.

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A New Determination of the E.M.F. of the Clark and Cadmium Standard Cells by Means of an Absolute Electrodynamometer.[1]

By K. E. Guthe.

THE method employed in this investigation was practically the same as the one described by Professor Patterson and the author a few years ago; but special attention was paid to an elimination of all errors which might possibly amount to more than one in ten thousand.

The electrodynamometer consisted of coils wound with a single layer of wire and of dimensions, first proposed by A. Gray, such that the length and radius are in the ratio of $\sqrt{3}:1$ to each other. The frame for the stationary coil was a hollow plaster of Paris cylinder, soaked in paraffine and very accurately turned on a boring mill. Its average diameter was determined by means of a large caliper of nickel iron and its coefficient of expansion taken into account in the calculations. The cylinder was wound with 872 turns of wire consisting of two separate coils, the turns of one being wound between those of the other, so that alternate wires belonged to different coils. This enabled us to measure the insulation resistance (40 megohms) of the whole apparatus after completion. The diameter of the stationary coil was close to 50 cm. and the length nearly 43.3 cm. The irregularity of the winding which was a little closer at the center necessitated a correction of somewhat more than one in one thousand.

In order to test the reliability of the results two movable coils of different dimensions were constructed, the larger having a diameter of 10 cm., the smaller of 7.5 cm. The porcelain cylinders, used as frames, were wound with 109 and 83 turns respectively, of bare copper ribbon, and the average diameters were measured by means of end comparators, reading to 0.001 mm.

The current was led into the movable coil through mercury cups and it was found necessary to slightly agitate the mercury during the observations in order to eliminate the disturbing effect of surface tension. The coils were carefully centered with their axes parallel and then the movable coil turned into position by twisting the torsion head by 90 degrees. Angles in the neighborhood of 90 degrees could be determined by means of a silvered glass cube whose angles had been measured accurately.

All materials used in the instrument were tested for magnetic permeability by means of a device, consisting of two induction coils, the induced electromotive forces in the secondaries being opposed to each other. The

[1] Abstract of a paper read at the meeting of the American Physical Society, December 29–30, 1905.

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material to be tested could be introduced inside of the primary of either coil. The permeability of plaster of Paris and porcelain differed not more than one in 100,000 from that of air.

It was decided after several unsuccessful trials with fused quartz, steel, platinum-iridium, carbon and other substances to use for a suspension a twelve year old phosphor bronze wire which showed a rather constant modulus of torsion and little elastic after-effect.

The modulus of torsion of the wire was determined by vibrating, suspended from it, gold plated cylinders of Tobin bronze whose masses and dimensions were accurately known. Two sets, each consisting of two cylinders of the same mass, but different shape, were used; the masses of the heavier set being equal to that of the larger movable coil and the cylinders of the other set weighing the same as the smaller coil. It was shown that the modulus of torsion of the suspension can be determined with sufficient accuracy from vibration experiments made with these cylinders and that it will keep constant enough during the time necessary for electrical determinations.

The standard cells were obtained through the kindness of Professors Carhart and Hulett. They were kept during the last weeks of the investigation within 0°.01 C. at 25° C. by means of a thermostat.

The cells were mostly cadmium cells, with electrolytically prepared mercurous sulfate (*E*, *F* and *O* series). Two cadmium cells contained chemically prepared mercurous sulfate (K_{10} and C_8) and three Clark cell (*R* series) were set up with electrolytic mercurous sulfate. The *F* series in which the mercurous salt was precipitated in an acid of concentration larger than molecular, the electromotive force is 0.00006 volt below that of the *E* and *O* series, and 0.00030 volt below that of the *C* series.

The electrical determinations consisted in sending the current flowing throw the electrodynamometer and balancing a torsion of the suspension equal to 90 degrees, through standard resistances and comparing the potential difference produced at their terminals with the electromotive force of the standard cells by means of a calibrated potentiometer. The elastic after-effect due to the twisting of the wire was taken into account.

The absolute value of the current was calculated from the formula

$$I^2 = \frac{\pi}{2}\frac{\tau}{AC}$$

where τ is the torsional moment for unit angle of the suspension, C the magnetic field in the center of the stationary coil, and A the effective area of the movable coil. In order to eliminate the effect of the earth's magnetic field and the possible influence of the lead wires it is necessary to take the geometric mean of four currents, obtained by reversing the current through the whole apparatus and for each of these two cases reversing the current in the movable coil.

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Seven complete determinations were made, three with the smaller and four with the larger coil. As reference standard an unsaturated Weston cell was used and its electromotive force at 21° C., was found, as shown in the table.

A. With smaller movable coil:	
Exp. 1.	1.01889 volts.
2.	1.01877 volts.
3.	1.01887 volts.
B. With larger movable coil:	
Exp. 4.	1.01886 volts.
5.	1.01885 volts.
6.	1.01887 volts.
7.	1.01880 volts.

From the comparison by means of the potentiometer method the electromotive force of the standard cells at 25° C., was found to be:

E.M.F. of the *F* cells (electrolytic) = 1.01827 volts.
E and *O* cells (electrolytic) = 1.01833 volts.
C cells (chemical) = 1.01857 volts.
R cells (electrolytic) = 1.42040 volts.

Reducing to 20° C., by assuming the temperature coefficient for the electrolytic cells to be the value accepted for those with chemically prepared mercurous sulphate, we find

E.M.F. of the *F* series at 20° C. = 1.01847 volts.
E.M.F. of the *C* series at 20° C. = 1.01877 volts.
and E.M.F. of the Clark cells at 15° C. = 1.43295 volts.

The electrochemical equivalent of silver, expressed by the author some time ago in terms of the electromotive force of a Weston cell, may now be calculated in absolute measure, since the cell used in the former work with the coulometer could be compared directly with the reference standard of this research. For a porous cup silver coulometer the electrochemical equivalent of silver, thus found, is

1.11774 mg. per coulomb.

Experiments on Resonance in Wireless Telegraph Circuits.[1]

By George W. Pierce.

THIS paper reports a continuation of experiments on the conditions for resonance in wireless telegraph circuits. Both the electromagnetically-connected type and the direct-connected type of circuits were studied, and a comparison of the two was made with respect to sharpness of resonance and the intensity of the signals received. The compari-

[1] Abstract of a paper presented at the New York Meeting of the American Physical Society, December 29, 1905.

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sons were made by measurements of the energy at the receiving station by methods described in the author's previous papers.

With the *electromagnetically-connected* circuits the "coefficient of coupling" of the circuits was varied by varying the mutual inductance between the two parts of both the sending and the receiving stations. The effect of such variation was found approximately to accord with the theory of inductive circuits; namely, with a decrease of the coefficient of coupling the capacity-hyperbola, described in the previous papers, approached its asymptotes, and the resonance became sharper. In an extreme case where the coefficient of coupling at the receiving station was .071 the resonance was so sharp that the energy received dropped to one half for a change of period of one and one half per cent.

With the *direct-coupled type of circuits* several methods of tuning were employed. In all cases the resonance was far less sharp than with the inductively connected circuits. For certain methods of tuning the direct-coupled type of circuit was shown to be a special case of the electromagnetically connected system.

In regard to the relation between the amount of energy received and the height of receiving antenna, the following approximate laws were obtained:

With a constant sending circuit and a constant source of waves,

I. *The current received in a direct-couple receiving circuit brought to resonance by a capacity in shunt is proportional to the square of the height of the receiving antenna.*

II. *When the receiving circuit is brought to resonance by an inductance in series with the instrument, the current in the receiving circuit is proportional to the height of the receiving antenna.*

These results are interesting in that they show entirely different laws for different methods of tuning. Therefore, the relation of height of mast to the distance to which signals may be sent (Marconi's Law, Braun's Law, etc.) will be dependent on the method employed in bringing the sending and receiving stations to resonance.

The paper also gives experiments on artificial grounds with a confirmation of the *image-theory* of the action of the ground. In the opinion of the author it is easy to construct an artificial ground superior to such natural grounds as may be effected by burying plates of metal in the earth.

Wave-lengths from 500 to 150 meters were employed in these experiments.

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Longitudinal Vibrations Analogous to those of a Violin String.[1]

By Harvey N. Davis.

THIS work was originally undertaken as the first step in an investigation of the effect of vibration on magnetic quality, an experiment in which it is desirable to maintain, in a steel wire, a steady state of vibration whose character and intensity can be fully determined and easily controlled. This has been accomplished by means of a mechanically operated rubbing-wheel, and a study of the resulting longitudinal vibrations has shown them to be identical in character with the transverse vibrations of a violin string. This fact gives them a considerable interest, quite apart from the specific use which is presently to be made of them, in that there is here presented a unique and exceedingly detailed experimental illustration of the parallelism between longitudinal and transverse vibrations which the mathematics of the subject predicts. Practically everything that has been observed for the violin string can be reproduced in the longitudinal case.

In two respects the present paper goes beyond the work of previous observers. In the first place, the fact that a given state of vibration can be kept up indefinitely and can be reproduced at will, has made it possible, for the first time, to measure amplitudes under conditions which are accurately known. This has resulted in a good quantitative verification of the established theory, and especially of the law connecting amplitude with bowing speed. The second of the contributions of the paper relates to the problem of solving the differential equation of vibrating strings subject to the peculiar kind of boundary conditions which the theory of the bowed string demands. The desired solution can be obtained in the form of a Fourier's series without difficulty, as Helmholtz first showed; but it is extremely difficult even in the simplest cases, and impossible in any but the simplest cases, to obtain from such a series any information as to the configurations of the string itself as it vibrates, or as to the nature of the motion of its individual points. To avoid this difficulty the author has devised a simple graphical method which will give this information in any case which the present state of the theory of bowed strings presents. Even in those simple cases which can be handled by the older method, the saving of time and of energy is so great as to be a matter of considerable importance to one

[1] Abstract of a paper presented at the New York meeting of the Physical Society, December, 1905. The paper will be published in the Proceedings of the American Academy of Arts and Sciences, and in the annual volume of the Jefferson Physical Laboratory of Harvard University.

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working in the subject. It is possible that this part of the paper will have some interest for the pure mathematician, for it is rather unusual that graphics should be able to give, not simply an approximate, but an exact and rigorous answer to a question which analysis is, as yet, unable to solve.

MAGNETIC AND ELECTRIC DEFLECTION OF THE α RAYS FROM RADIUM.[1]

BY E. RUTHERFORD.

THIS paper contains a preliminary account of experiments made to determine with accuracy the ratio e/m of the α particles projected from radium. The α rays from radium are complex and consist of particles projected with very different velocities. Such a source of rays is not suitable for accurate measurement, as the rays are unequally deflected in electric and magnetic fields.

This difficulty was overcome by using an active wire exposed for some hours to the radium emanation as a source of rays. Fifteen minutes after removal, radium *A* has been almost completely transformed, and the activity is then due almost entirely to radium *C*. Previous experiments by the author (Phil. Mag., July, 1905) have shown that such an active wire serves as a homogeneous source of α rays. The layer of active matter on the wire is extremely thin, and the α particles are all projected from the wire at the same speed.

The magnetic deflection of the α rays was measured by a method similar to that described in a previous paper (loc. cit.). The electric deflection was determined by the photographic method. The rays passed between two parallel plates 3.75 cm. long and .21 mm. apart. A photographic plate was placed about 4 cm. above the plates. The apparatus was then exhausted by a mercury pump, and a known voltage applied between the plates. The active wire was placed outside the apparatus, the rays entering the vessel through a thin mica screen of known thickness. The electric field was reversed at intervals. For weak fields, the narrow trace of the rays on the plates was first broadened; with stronger fields, the single band broke into two, each narrower than the normal width of the band without an electric field. The outside edges of the bands were clearly defined, and the distance between the outer edges could be readily measured.

In this arrangement, the parallel plates served to determine the width of the pencil of rays, as well as to apply the electric field. Since the plates were close together, a field corresponding to 20,000 volts per cm.

[1] Communicated to the American Physical Society, December 29, 1905.

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could be obtained with 400 volts between the plates, without any danger of a discharge, even if the vacuum were not very good.

From the distance between the outside edges of the two bands, the value of mv^2/e could be calculated. The value of mv/e was determined in the magnetic experiment by measuring the curvature of the path of the rays after passing through the same thickness of mica as in the electric experiment.

The determinations of e/m and v for different strengths of electric and magnetic fields were very concordant. The values of e/m in the different experiments lay between 5.0×10^3 and 5.2×10^3. A separate experiment showed that the value of e/m was unaltered by passing the rays through the mica screen.

The initial velocity of projection of the rays from radium C is very nearly 2×10^9 cm. per second.

The writer originally obtained by the electric method a value of e/m for radium rays of 6.5×10^3; Des Coudres by the photographic method found a value 6.3×10^3, while Mackenzie recently obtained a value of 4.7×10^3. These experimenters all used radium in radioactive equilibrium as a source of α rays. The rays were non-homogeneous, and it was consequently not easy to obtain an accurate value of e/m.

Since the value of e/m for the hydrogen atom in the electrolysis of water is about 10^4, the present results show that, within the limit of experimental error, the apparent mass of the α particle from radium c is twice that of the hydrogen atom.

The question whether the α particle is a molecule of hydrogen, an atom of helium, or a helium molecule carrying twice the ionic charge, was discussed. It is not at present possible to decide definitely between these possibilities. Further experiments are in progress to determine the value of e/m for the α particles from the other radium products and from thorium and actinium.

Some Properties of the α Rays from Radium. II.[1]

By E. Rutherford.

In the Philosophical Magazine (July, 1905), the author showed that the α particles emitted from a thin film of radium C, obtained on a wire by exposure to the radium emanation, decreased in velocity in their passage through matter. When the α particles from radium C had been reduced to a velocity of about 60 per cent. of their initial velocity, the photographic effect produced by them was relatively very small.

The velocity was deduced from measurements of the deflection of a

[1] Communicated to the American Physical Society, December 29, 1905.

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pencil of the α rays in a strong magnetic field, using the photographic method. The results confirmed the essential points of the theory of Bragg and Kleeman of the nature of the absorption of the α rays by matter. The rays from radium are complex and consist of four sets of α rays from the four α ray products, each set of rays being initially projected with a definite but different velocity.

In a recent paper, Becquerel (Comptes Rendus, Sept., 1905), has taken exception to these views. He states that the α rays from radium are homogeneous, and that their velocity is not reduced by their passage through matter, and concludes that the theory of Bragg and Kleeman is incorrect.

In support of his views, Becquerel describes an experiment in which the trace of the α rays from a thick layer of radium was not altered by placing absorbing screens over the radium.

The author showed that the result obtained by Becquerel is a necessary consequence of the view that the rays are complex, and does not in any way invalidate the conclusions of Bragg and Kleeman and Rutherford. The outside edge of the trace of the pencil of rays on a photographic plate, when exposed in a magnetic field, is due to the α particles which are just able to produce an appreciable effect on a photographic plate. When a screen is placed over the radium, the velocity of all the particles is reduced, but, as before, the outside edge of the trace will be produced by rays which, after emerging from the screen, have the same velocity as in the first case. The deflection in a magnetic field will consequently be unaltered, and there will be no apparent displacement of the trace of the rays, although the velocities of the α particles as a whole are reduced in their passage through matter.

The inside edge of the trace should be slightly altered but this effect would be too small to detect experimentally under the conditions of the experiment of Becquerel.

It was also shown that the α rays from a thick layer of radium are deflected to unequal extents by a magnetic field. This dispersion of the rays in a magnetic field shows that the α particles are expelled from radium over a wide range of velocity. The position taken by Becquerel, viz., that the α rays are all projected at the same speed, is untenable.

Becquerel observed that the radius of curvature of a pencil of rays emitted from radium was not constant but increased with distance from the source. The explanation of this effect has been given previously by Bragg, and has been shown to be a necessary consequence of the complexity of the α rays. The assumption made by Becquerel that the ratio e/m decreases with distance from the source of rays is unnecessary. In addition, the author showed that the magnetic deflexion of the α rays from radium C increased when the rays passed through air instead of a

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vacuum. According to the views of Becquerel, the amount of deflexion of the α rays under such conditions should be reduced by their passage through air.

The results in general completely support the theory of Bragg and Kleeman that the α rays from radium decrease in velocity in their passage through matter, and disprove in every particular the theories proposed by Becquerel.

On the Use of Centrifugal Force in Soil Investigations.[1]

By Lyman J. Briggs.

CENTRIFUGAL force can be employed with advantage in the following laboratory investigations of soils:

1. The study of the retentive power of different soil types for moisture. The moist soil is placed in a perforated cup and subjected to a known centrifugal force, by which the moisture content is reduced until it is in equilibrium with the force employed. It logically follows that two soils whose moisture contents have thus been brought into equilibrium with the same force should, when placed in contact, be in capillary equilibrium. The method thus enables us to determine the moisture equivalents of different soil types, which it is essential to know before the moisture contents of two soils under field or laboratory conditions can be rationally compared.

2. The study of the rate of movement and the final distribution of moisture in a column of soil when acted upon by a known force. In this case the tube containing the moist soil is mounted radially on a shaft revolving at a known rate. The method gives a means of determining the moisture gradient necessary to maintain equilibrium against a uniform force gradient. By the arrangement of the apparatus so that water can be supplied at a definite rate, the moisture gradient necessary to maintain a steady flow of known amount under the influence of a given force gradient can be determined. The direction and rate of movement of soil moisture under field conditions can then be determined from a study of the moisture distribution in the field. These methods have not yet been tried experimentally.

3. The study of the composition and concentration of the soil solution. A part of the soil moisture with the substances it holds in solution can be removed by centrifugal force without changing, so far as we have been able to determine, the composition or concentration of the soil solution. This method possesses obvious advantages over the excess-solvent

[1] Abstract of a paper presented at the New York meeting of the Physical Society, December 29–30, 1905.

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methods, in which the relatively large amounts of solvent used affect the equilibrium of the soil solution.

4. The study of the mechanical composition of the soil. The mechanical composition is found by separating the soil grains into arbitrary groups according to size, by taking advantage of the different rates of subsidence of the soil particles in water. The use of centrifugal force is of much assistance in hastening the subsidence.

AN ELECTRICALLY CONTROLLED THERMOSTAT OPERABLE AT ROOM TEMPERATURES.[1]

BY LYMAN J. BRIGGS.

MOST thermostats heretofore described have been designed to operate either above the maximum or below the minimum room temperature, so that their regulation could be effected by the control of either a heating or a cooling system. The form described in this paper will operate satisfactorily, even though the temperature of the room may be constantly fluctuating above and below the temperature of the thermostat. The heating is effected by an electric heater, and the cooling by tap-water or ice-water according to the requirements, the flow being regulated by an electrically controlled valve.

Acetone, which has a cubical coefficient of expansion of about two fifths that of air, is used in the temperature regulator. The expansion of this liquid controls the height of a mercurial column *in vacuo*. Two small platinum wires are sealed into the glass tube containing the mercurial column at a distance of about one centimeter above the mean barometric height, one wire being about one millimeter above the other. The relay which opens the heating circuit is operated by the mercury column being brought in contact with the lower wire, while the relay controlling the cooling system is operated by the mercury coming in contact with the upper wire. *The exhaustion of the air from above the top of the mercury column keeps the contact surfaces clean and bright.*

The thermostat operates on the heating or the cooling circuit according as the temperature of the room is lower or higher than the desired temperature of the thermostat. The 110-volt heating circuit is controlled directly by the relay, arcing being prevented by connecting a 2-microfarad condenser across the contact points. The relay operating the cooling system has a two-point control, one for closing and the other for opening the valve. The valve is so arranged that when it is turned to its position of maximum flow, the circuit of the motor controlling it is

[1] Abstract of a paper presented at the New York meeting of the Physical Society, Dec. 29–30, 1905.

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automatically broken, and the motor is connected with the closing point of the relay. When the tank has been sufficiently cooled and the relay armature is released, the motor again operates until the valve is closed, when the circuit is again automatically broken and the motor connected with the opposite point of the relay.

The glass bulb containing the acetone is about 2.5 cm. in diameter and 40 cm. long, while the diameter of the mercurial column is 1.6 millimeters. This regulator has been found to maintain the temperature of a bath containing 400 liters of water constant to within less than one fiftieth of a degree C. There is considerable lag in the temperature of the acetone in a bulb of this form, and the sensibility could undoubtedly be made greater for the same volume of liquid by increasing the length of the bulb. It is necessary in using acetone to protect the grease upon the stop-cock by means of a mercury seal, which is easily done by introducing a short U-tube between the bulb and the stop-cock.

An Attempt to Explain the Cause of the Pressure-Shift and the Broadening of Spectrum Lines.[1]

By W. J. Humphreys.

FROM the experimental work of J. J. Thomson, Zeeman, and others, it is assumed that an atom, at least when luminous, possesses a magnetic field of its own, due to ions rotating in closed orbits. These atoms by rushing to and from each other, will through induction increase and decrease the periods of ionic rotation. There will be Zeeman effects, the atoms themselves furnishing the magnetic fields. This leads naturally to the production of lines of finite width, which width will increase with increased density. It also leads to a shift of the lines as a whole to the *red* end of the spectrum, and in a manner quite in accord with experimental observations.

This explanation of spectroscopic phenomena is offered only as a working hypothesis, suggestive of valuable experimentation.

The Mount Weather Research Observatory.[1]

By W. J. Humphreys.

THE vast economic importance of weather forecasts makes it imperative that their accuracy and range be made as great as possible. The U. S. Weather Bureau has, therefore, begun the construction of a group of observatories and laboratories to be devoted to investigations that

[1] Abstract of a paper presented at the New York meeting of the Physical Society, Dec. 29–30, 1905.

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bear on meteorological problems. These consist chiefly of a weather station, now equipped and in use; a balloon and kite plant, about ready for work; two buildings devoted to the study of terrestrial magnetism, the equipment of which is now being installed; a physical laboratory, in course of construction; and a solar physics observatory, for which plans are being considered.

All these buildings are situated on the same reservation, on the crest of the Blue Ridge, in Northern Virginia, away from the dust of cities, and the jars of traffic.

Any thing that bears directly or indirectly on meteorological problems will be regarded as a fit subject for investigation; and each investigator will be given full credit for that which he himself has done.

It is earnestly desired that the relation between this observatory and other institutions shall be one of mutual helpfulness, and much has already happened to encourage us in the belief that this desire will be fulfilled.

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THE

PHYSICAL REVIEW.

ON THE CONDITIONS FOR SPARKING AT THE BREAK OF AN INDUCTIVE CIRCUIT.

By J. C. Hubbard.

Introduction.

LORD RAYLEIGH has discussed the relation existing between the energy given to the secondary of an induction coil when the primary current is broken and the velocity of separation of the contacts of the break of the primary.[1] He showed qualitatively, breaking the primary circuit by means of a rifle bullet, that in some cases a greater potential was produced in the secondary than when an ordinary break was used with its *optimum* capacity, and he came to the conclusion that if the break were made with sufficient abruptness, we might do away with the primary condenser altogether.

By optimum capacity is meant that capacity which, when put in parallel with the break of an inductive circuit, is sufficient, and just sufficient, to prevent a spark at the break, when the circuit is broken in a given manner.

We may sum up the chief results of experience in this connection under the following heads:

1. For a given break and primary current there is a given optimum capacity. Walter[2] has shown very clearly by means of figures obtained with a Braun tube that the fall of current in the primary, and therefore the rise of the induced potential, is most

[1] Phil. Mag. (6), 2, p. 581, 1901; Papers, Vol. IV., pp. 564–8.

[2] B. Walter, Ueber die Vorgänge im Inductionsapparat, Wied. Ann., 62, p. 300, Sept., 1897; and 66, p. 623, Nov., 1898.

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rapid when the capacity in the primary has been brought to the least possible value without causing the primary break to spark. As the capacity is diminished, the induced potential rises until values are reached so large as to cause an arc to form at the break retarding the rapidity of fall of the current.

2. For larger values of the primary current the optimum capacity is larger. That is, a greater capacity is necessary to prevent a spark.[1]

3. For a given primary current a great increase of abruptness of breaking the circuit diminishes the necessary primary capacity (Lord Rayleigh).

Since the induced potential is proportional to the primary current and inversely to the square root of the capacity it is clear from the foregoing that to get the best possible secondary potentials we must have the largest possible primary currents and the least possible primary capacity, and in order to realize these conditions it is necessary to have the most abrupt possible break.

With a view to determining quantitatively the relation existing between these quantities, J. E. Ives undertook a series of measurements,[2] but he was led to experiment with values of the current so small that he did not succeed in finding the desired relation.

The present paper is an attempt to establish the relation which exists between the rapidity with which the break contacts are pulled apart, or the *velocity of break*, as we shall call it, and the constants of the system together with the primary current, *for a single circuit;* for the results may easily be extended (see supra) to induction coils by the consideration of principles laid down by B. Walter.

THEORETICAL.

Consider the processes going on in an inductive circuit immediately following an interruption of the current. As the lines of magnetic force due to the current disappear, an induced electro-motive force causes a spark at the break, provided the contacts have not become sufficiently separated to prevent it. This spark represents

[1] Walter, loc. cit.; T. Mizuno, On the Function of the Condenser in an Induction Coil, Phil. Mag. (5), 45, pp. 447–454, 1898. K. R. Johnson, On the Theory of the Function of the Condenser in an Induction Coil, Phil. Mag. (5), 49, pp. 216–220, 1900.

[2] PHYS. REV., Vol. XV., No. 1, p. 7, 1902.

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a waste of energy and retards the fall of the current. If the velocity of separation of contacts, or the velocity of break, be great enough to prevent a spark, the current will fall to zero with a rate dependent upon its own initial value and the constants of the system.

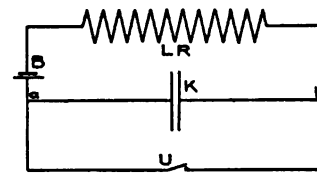

Fig. 1.

Let a circuit be connected as shown in Fig. 1. LR is a coil of inductance L and resistance R. It is connected in series with a battery of electro-motive force E and a break U. Across the break is connected a condenser of capacity K. We wish to find a relation, if any exist, between the velocity of break, the initial current, and the constants of the system when the conditions are just sufficient to prevent sparking at the break.

We have for the equation of the current, on the assumption that there is no spark,

$$L\frac{d^2I}{dt^2} + R\frac{dI}{dt} + \frac{I}{K} = 0,$$

which, with the initial conditions,

$$t = 0, \qquad I = I_0, \qquad Q = 0.$$

where Q is the charge on the condenser, has for its solution

$$I = I_0 \frac{2\sqrt{L}}{\sqrt{4L - R^2K}} e^{-\frac{R}{2L}t} \cos\left\{\sqrt{\frac{1}{KL} - \frac{R^2}{4L}} \cdot t - \tan^{-1}\sqrt{\frac{R^2K}{4L - R^2K}}\right\}.$$

In the experiment which we shall consider K is of the order 10^{-9} farads, L is 1 to 3 henries, and R is 50 to 200 ohms; accordingly, to an approximation having far greater accuracy than we can reach, experimentally,

$$I = I_0 e^{-\frac{R}{2L}\cdot t} \cos\left(\frac{t}{\sqrt{KL}}\right).$$

This equation was used by B. Walter in his experiments with the induction coil.

We have also

$$V = E + L\frac{dI}{dt} - RI,$$

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giving

$$V = E + I_0 \sqrt{\frac{L}{K}} \sin\left(\frac{t}{\sqrt{KL}}\right).$$

Since we are dealing with induced electromotive forces of from a few hundred to many thousands of volts we may neglect E, which was usually about two volts. It is clear that the spark, if it takes place at all, will occur some time before the first maximum of potential is reached. Using the above values for the constants of the circuit, the exponential factor $e^{-\frac{R}{2L} \cdot t}$ will have a value of about .99 at the end of the first quarter period. We therefore have, to an approximation of about one per cent.,

$$V = I_0 \sqrt{\frac{L}{K}} \sin\left(\frac{t}{\sqrt{KL}}\right).$$

We consider now the action of this potential in producing a spark at the break, assuming that the contact surfaces are portions of spheres of large radius in comparison with sparking distances.

In the first place, we have a rapidly varying potential. Does a varying potential follow the law which connects a constant potential with its spark length? There has been much controversy on this point. Jaumann[1] maintained that the spark length for a varying potential does not depend upon the value of the potential at the instant of sparking but upon the value of VdV/dt. As J. J. Thomson has pointed out,[2] his experiments may be brought into accord with the law for constant potentials by considering the electric waves set up in the system. Some work of Warburg[3] seems to settle the question, for he shows that within limits potential changes are without influence on the sparking constants, provided the gas is ionized.

Further, there is the question of the lag effect on the spark length. Jaumann[4] showed that there is an interval between the time of application of the potential and the time of sparking, during which some

[1] Wied. Ann., 55; p. 656, 1895.
[2] Conduction of Electricity through Gases, p. 351.
[3] Wied. Ann., 62, p. 385, 1897; Ann. d. Phys., 5, p. 818, 1901.
[4] Loc. cit.

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process goes on in the gas which changes it into a conductor. J. J. Thomson applied without causing a spark a potential several times the sparking value to a spark gap in carefully dried air. The complete determination of the lag effect would require more knowledge than we have at present of the growth of ionization produced by an electric field. According to J. J. Thomson's theory of the spark discharge[1] when a sufficiently great difference of potential is applied to a spark gap, ions initially present are driven with great enough velocity to produce fresh ions by collision with molecules of the gas. These new ions produce ions in their turn and the ionization and accordingly the conductivity of the gas will increase in geometric progression until the spark takes place. The duration of the lag will depend on the number of ions initially present. The lag is much diminished by any ionizing agency, such as ultra violet light, or the spark itself.

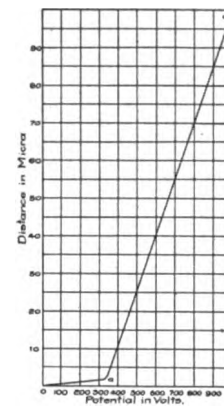

Fig. 2.

Earhart[2] has obtained values of the sparking potential for small distances between spherical surfaces in air. The relation is shown in Fig. 2 taken from Earhart. For distances from zero to .003 mm. the potential is proportioned to the distance (*oa*, Fig. 2). Here the spark potential, $V_s = gx$, where g is about 1.2×10^6 volts per cm. The curve changes abruptly between $x = .003$ mm. and $x = .01$ mm. after which it follows the law $V_s = ax + b$, where a is about 70,000 volts per cm. and b is less than the minimum spark potential, 351 volts. In this paper we shall deal only with the branch of the curve *ad*, Fig. 2, where $V_s = ax + b$. We shall assume the equation to hold regardless of variations of potential, and endeavor to find by means of deviations from it some indication of the magnitude of the lag effect in the cases under consideration.

We have then, as the limiting conditions for sparking,

$$V_s = V$$

and

[1] Phil. Mag. (5), 50, p. 278, 1900.
[2] Earhart, Phil. Mag., VI., 1, p. 147, 1901.

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$$\frac{dV_s}{dt} = \frac{dV}{dt},$$

also, $x = vt$, where v is the velocity of break. Therefore,

$$avt + b = I\sqrt{\frac{L}{K}} \sin \frac{t}{\sqrt{KL}},$$

and

$$av = \frac{I}{K} \cos \frac{t}{\sqrt{KL}}$$

where I is the initial current. Eliminating t,

$$av\sqrt{KL} \cos^{-1}\frac{avK}{I} + b = I\sqrt{\frac{L}{K}}\sqrt{1 - \left(\frac{avK}{I}\right)^2}.$$

In the present experiments $avK/I = Z$ was seldom as much as .4, that being one of the largest values recorded.

We have

$$\cos^{-1} Z = \tfrac{1}{2}\pi - Z - \frac{Z^3}{6} \cdots,$$

$$(1 - Z^2)^{\frac{1}{2}} = 1 - \tfrac{1}{2}Z^2 - \tfrac{1}{8}Z^4 \cdots.$$

Neglect of higher powers of Z than the second will cause an error under one per cent. Accordingly

$$av\sqrt{KL}\left(\frac{\pi}{2} - \frac{avK}{I}\right) + b = I\sqrt{\frac{L}{K}}\left[1 - \frac{1}{2}\left(\frac{avK}{I}\right)^2\right],$$

or

$$\frac{\pi}{2} \cdot \frac{avK}{I} - \frac{1}{2}\left(\frac{avK}{I}\right)^2 + \frac{b}{I}\sqrt{\frac{K}{L}} = 1.$$

As a first approximation

$$\frac{\pi}{2} \cdot \frac{avK}{I} + \frac{b}{I}\sqrt{\frac{K}{L}} = 1.$$

Solving for avK/I and substituting its square in the first equation,

$$\frac{\pi}{2}\left(\frac{avK}{I}\right) = 1 - \frac{b}{I}\sqrt{\frac{K}{L}} + \frac{2}{\pi^2}\left(1 - \frac{b}{I}\sqrt{\frac{K}{L}}\right)^2$$

whence

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$$v = \frac{2I}{\pi aK}\left(1 + \frac{2}{\pi^2}\right) - \frac{2b}{\pi a\sqrt{KL}}\left(1 + \frac{4}{\pi^2}\right) + \frac{4b^2}{\pi^3 aIL}.$$

or

$$(1) \qquad v = .7656\frac{I}{aK} - .8946\frac{b}{a\sqrt{KL}} + .1290\frac{b^2}{aLI},$$

the equation connecting the velocity of break with the constants of the system and the initial current, which we shall use in connection with the experiments.

We may write the first approximate equation thus:

$$v = \frac{2}{a\pi\sqrt{KL}}\left(I\sqrt{\frac{L}{K}} - b\right),$$

showing that the velocity of break necessary to prevent a spark is roughly proportional to the requency and to the excess of the maximum potential over the minimum spark potential.

Experimental Arrangements.

The apparatus was usually arranged in the following manner: An inductance, LR, storage cell, B, interrupter U, and box resistance R_b, were connected in series as shown in Fig. 3. A condenser K of variable capacity is joined in parallel with the box resistance and break. The purpose of this resistance is to permit variations of current without affecting thedamping factor. A quadrant electrometer is connected idiostatically with the terminals of the condenser. The inductance used has been described by J. E. Ives.[1] It was wound in a series of six coils in a large flat wooden spool. The total inductance is 3.01 henries. About two miles of wire was used, having a resistance of 62.18 ohms. A bridge circuit, not shown, was arranged for the purpose of measuring the resistance of various parts of the circuit, or of all together, at will. The terminal of the condenser next the battery was kept to earth at E. The capacity of the system is that of K with one of its plates to earth, together

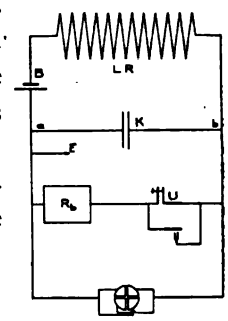

Fig. 3.

[1] J. E. Ives, Phys. Rev., XIV., p. 298, 1902.

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with the capacity of its leads, of the break with its contacts apart and its leads, and the unknown, and in these experiments unmeasured capacity of the coil due to the oscillations of the potential. The capacity of the coil is probably negligibly small in comparison with the external capacity, the more so, as Drude[1] has shown that the capacity of a coil vibrating in its natural period is lessened with the addition of end capacity.

For a break was used one of the contact levers of Dr. Webster's drop chronograph.[2] The lever is so adjusted that when the break is closed the end which is struck by the falling weight is on a level with the pivot, ensuring that the velocity of the end when struck, in the direction perpendicular to the radius is equal to the velocity of the falling weight. The velocity of break is then equal to $r\sqrt{2gh}$ where $\sqrt{2gh}$ is the velocity of the projectile and r is the ratio of the length of the arm carrying the contact to the length of the arm struck having the value .479.

MEASUREMENT OF CAPACITY.

The most trouble encountered in the experiments was in connection with the measurements of capacity. The capacity of the system is of the order 10^3 cm. which is difficult to measure electrostatically with a great degree of accuracy. The method of measurement adopted was suggested by Dr. Webster. K_2 (Fig. 4) is a standard condenser. K_1 is the system the capacity of which is to be measured. The part of the system which was connected to earth in the oscillation experiments is the upper part of K_1, which together with the upper side of K_2 may be connected to earth at E_1, at a, but always connected with the electrometer. A steady current flows from a large number of storage cells B through R_1 and R_2 between which is an earth connection, E_3. A commutator connects 2 with

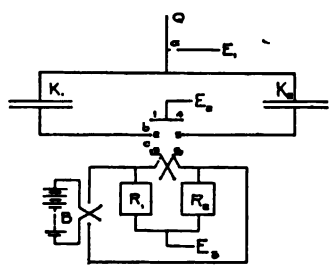

Fig. 4.

[1] Drude, Ann. d. Phys., 314, p. 293, 1902.

[2] A. G. Webster, An Experimental Determination of the Period of Electrical Oscillations, PHYS. REV., VI., p. 300, 1898.

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3, and 5 with 6, at c. The lower plates of K_1 and K_2 are thus at potentials proportional to R_1 and R_2. Equal and opposite charges are induced on the opposite branches of the system. If, now, the earth connection at a be broken and the commutator rocked so as to connect 1 with 2 and 4 with 5 at b, the charges on the lower plates run to earth at E_2 and, if the charges on the upper plates be equal, no deflection in the electrometer will result. Then will

$$\frac{K_1}{K_2} = \frac{V_2}{V_1} = \frac{R_2}{R_1}.$$

All possible precautions were taken to insure perfect insulation. All connections were of copper, as it was found that the use of mercury connections introduced serious error, as from heating by a nearby lamp, or mechanical agitation, producing thermo-electric effects. It was found necessary to cement all binding posts to glass with sealing wax and to have them sufficiently removed from other conductors to make their capacity negligible. The switches and commutator were made of small metallic parts embedded in beeswax or paraffine. On dry days it was found possible and easy to measure capacities of 10^3 cm. to 1 cm. The resistances were reversed, the direction of current was reversed and various points of connection were shifted without causing changes greater than those observed when the conditions were kept the same. On damp days it was found possible to measure capacities only after all connections had been carefully gone over with a jet of air which had been passed through a quantity of concentrated H_2SO_4. To test the method different lengths of parallel wires were connected to K_1 and the increase in capacity thus produced agreed with that calculated to 1 cm.

The variable capacity consisted of two plates, the upper one being in the form of a small plate with a guard ring which were connected together so as to act as one plate with a diameter of 18 inches. This plate was supported at the edge upon ebonite pillars which rested upon a rigid iron frame work. Beneath this was the other plate, 16.5 inches in diameter, supported by a large screw which, by means of a nut at the base of the instrument, could be raised or lowered without rotation. The screw threads were 20 to the inch.

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One revolution of the nut from the position which gave contact (not taken as the zero) gave 820 cm. capacity.

The standard condenser has been fully described by Dr. Webster.[1] The lower plate was supported upon three rigid, ebonite tipped legs. On top of the plate, directly over its points of support, were placed three small glass cylinders, of accurately known length, and upon these was set the top plate. The condenser was kept throughout at some distance from the other apparatus, and at about 5.5 feet distance from the floor and eight feet from the nearest wall. On the approach of a person as closely as possible without touching, the condenser showed a change of capacity of about one fourth per cent.

It is of course necessary to keep the form of all circuits, connections, and apparatus the same during measurements of capacity as they are kept when experiments are made in which use is to be made of capacity measurements. There must be no electrometer deflection when the earth connection at a is broken, whether K_1 or K_2 is connected in alone, or both together. This was the test for leakage in the capacities. We are thus able to measure with considerable accuracy all the capacity effective in the oscillation experiments with the exception of that due to the coil. The variable condenser was calibrated. On the addition of the electrometer with its leads the increase of capacity was found to be 13 cm. On the addition of the leads to the break the increase was 12 cm. In the oscillation experiments, accordingly, the reading of the condenser screw was taken, the capacity found from the calibration curve, and 25 cm. added. This was occasionally verified by the measurement of all together.[2]

An example is here given of the magnitude of the changes produced in the capacity measurements when the currents and resis-

[1] Loc. cit.

[2] A slight modification of the above method enables us to measure the capacity of a small body with reference to all surrounding bodies taken together. Put a at E_1 permanently to earth, and make the electrometer connection at E_2. Then when the commutator is rocked after disconnecting E_2 from earth, if the charge on the lower parts of K_1 and K_2 are equal no deflection will result. A spherical acoustical resonator of 23 cm. diameter, having a slight projection on one side, was supported at a distance of three feet from all other conductors. It was put in connection with the lower side of K_1. The observed increase in capacity was $12 \pm .25$ cm.

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tances were reversed. The nut of the variable capacity was turned .588 revolution from zero position. Twenty storage cells were used in the battery.

	R_1	R_2	R_2/R_1
	640.5	1,000.0	1.5613
Current reversed.	639.5	1,000.0	1.5637
	1,000.0	1,565.5	1.5655
Current reversed.	1,000.0	1,565.5	1.5655

$$K_2 = 826.5 \text{ cm.} \quad K_1 = \frac{R_2}{R_1} K_2 = 1{,}293 \text{ cm.}$$

The following experiments do not call for this degree of accuracy and it might seem that the large amount of time spent upon the capacity measurements was lost, but in such work a very small amount of leakage causes indefinitely large errors and care had to be taken that everything of the kind should be eliminated.

A proof of the relative correctness of the calibration of the variable condenser is found in the fact that the calibration curve is a very smooth one and follows the formula

$$K = \frac{c}{d + e}$$

over a long range, c being a constant, d is the reading of the screw from zero position and e is a small correction to be added to d for the reason that the plates, owing to imperfect surfaces and lack of parallelism did not everywhere touch when $d = 0$. Part of the calibration is here given to show the agreement between measured values of K and those calculated from the above formula, using $c = 863.5$ and $e = .080$.

d	K Meas.	K Calc.	Diff.
.610	1,252	1,252	0
.660	1,170	1,167	−3
.720	1,079	1,079	0
.800	980	982	+2
.890	891	890	−1
1.000	799	799	0

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The formula takes no account of the thickness of the plates or of the metallic frame work.

METHOD OF TAKING READINGS.

In finding the values of velocity of break just sufficient to prevent sparking, the apparatus was connected as in Fig. 3. When the circuit is broken at U, there will result oscillations of potential in the condenser and at the break which are measured by the electrometer, connected as shown. The drop, in continuing its fall, after breaking the circuit closes it again by means of another lever, indicated in the figure, after the potential oscillations have died away, but in so short a time as to eliminate the effect of the battery e.m.f. on the readings of the electrometer. The latter are then proportional to the time integral of the square of the induced potential. In all the following experiments except the first, the constants of the circuit were kept the same in each set while the current was varied. The electrometer readings, provided there is no spark, will then be proportional to the square of the initial current.

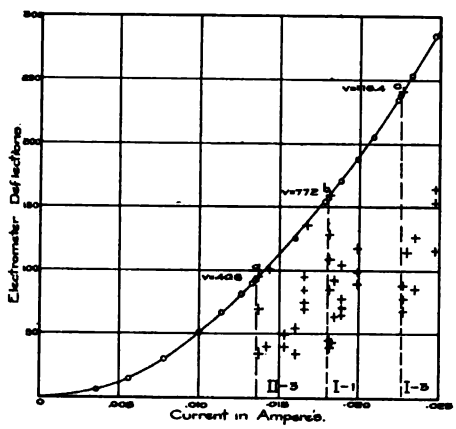

Fig. 5.

Imagine the projectile of the drop chronograph hung at a distance h above the contact lever of the break. Each interruption of the current caused by the fall will be made with the same velocity of break. Make R_b very large so as to cause a small current to flow through the inductance when the circuit is closed. If the drop is allowed to fall, a definite deflection will result, and will be the same for every fall if there is no spark. Let smaller values of R_b be chosen, so as to increase the initial current. There will be continuously larger electrometer deflections, and the curve plotted from initial currents and electrometer readings (see Fig. 5) will be parabolic in form as long as no sparking takes place. As

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we go on increasing the initial current we at length come to a point (at *a*, for instance) beyond which the electrometer readings fall short of the curve and differ among themselves by several hundred per cent. An examination of the break reveals the fact that a small spark takes place at each interruption. The region of this discontinuity was carefully explored. The limiting value of the current is taken as the largest value of the current which will give five successive electrometer readings on the curve when the circuit is broken. This rule was adopted both to eliminate personal judgment from the results, and because it was often found possible by careful polishing of the break contacts to get sparks after two or three readings had been taken which lay on the curve, showing that the critical value had not been reached. Points somewhat separated were chosen for Fig. 5, so as to show the regions explored without overlapping.

The following table for the exploration of the neighborhood of a point of discontinuity (*c*, Fig. 5) will show in what manner the limiting values of the current corresponding to velocities of break were chosen. The last two rows of figures give the number of readings on and off the curve, respectively,

$K = 585$ *cm.* $L = 3.01$ *henry.* $R = 62.2$ *ohms.* $h = 30.02$ *cm.* $v = 116.4$ *cm./sec.* $E = 2.029$ *volts.*

R_b	10	20	24	26	27	27.5	28
I.	.02816	.02471	.02354	.02302	.02278	.02263	.02253
No spark.	0	0	0	0	3	5	5
Spark.	2	3	2	1	3	0	0

giving $I = .02272$ ampere, corresponding to $R_b 27.3 \pm 2$ (see supra, series 1–3). The velocities corresponding to *a* and *b* of the curve were respectively 40.8 (series II. — 3), and 77.2 cm./sec. (series I. — 1).

Values obtained in this way were supplemented by direct observations at the spark gap and were always verified. It was thus possible to determine the limiting values of the current to one per cent. The electrodes of the break were carefully polished with a silk cloth after each reading. The electromotive force of the battery was measured whenever a limiting value of the current had been

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reached, and the resistance of the entire circuit including the break, closed, was found at the same time. Occasional verifications of the magnitude of the capacity were made. The switch for releasing the drop and the telescope for reading the electrometer, as well as the commutator for the purpose of bringing its needle to rest were placed on a table at a distance of several feet from the oscillation circuit.

PRELIMINARY EXPERIMENT.

Connection Between Optimum Capacity and Velocity of Break.

An experiment was first undertaken to ascertain suitable values of the quantities involved for the purpose of later work. The system was set up as in Fig. 3 omitting R_b. The variable capacity was made large and gradually diminished until the electrometer readings on breaking the circuit at a definite rate ceased to be a continuous function of the capacity. The region of discontinuity was explored, much as described in the previous section. The optimum capacity was chosen as the least capacity which gave five successive readings which lay on the capacity-deflection curve. The experiment was undertaken before much progress had been made with the measurements of capacity and the accuracy of the latter is probably not much greater than five per cent. The following table gives the values of the optimum capacity with the corresponding velocities of break:

$L = 3.01$ *henry.* $R = 63$ *ohms.* $R_b = 0.$ $E = 2.02$ *volts.* $v = r\sqrt{2gh} = 21.2\sqrt{h}.$

h cm.	v cm./sec.	K cm.
69.1	176.2	670
15.5	83.5	1,160
4.8	46.4	1,780
1.11	22.3	4,170

The curve got by plotting K and v is almost hyperbolic in form (Fig. 6) showing that for a given current the optimum capacity is nearly inversely as the velocity of break.

If we put for equation (1) when K is in farads

$$v = \frac{A}{K} - \frac{B}{\sqrt{K}} + C$$

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we get from the above data,

$$A = 238{,}000.$$
$$B = 6{,}270.$$
$$C = 66.4.$$

Where

$$A = .7656\frac{I}{a}; \quad B = .8946\frac{b}{a\sqrt{KL}}; \quad C = .1290\frac{b^2}{aL}.$$

From A,

$$a = 92{,}800 \text{ volts/cm.}$$

from B and a,

$$b = 1{,}190 \text{ volts.}$$

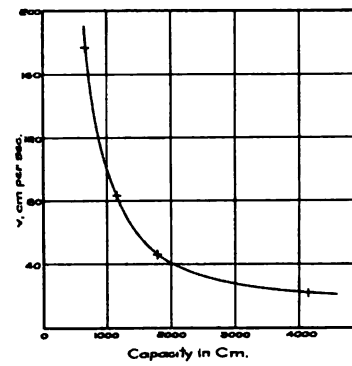

Fig. 6.

The value of a as obtained by Earhart is, as we have seen, about 70,000 volts/cm., while that of b is 351 volts. The agreement for a is perhaps as good as could be expected in view of the small number of readings, the errors of capacity measurements, and the neglect of the lag effect.

Experimental Results.

The following results were obtained by the method described in the last article but one. The capacities were measured with an accuracy of from one tenth to one third per cent., not including the capacity of the coil. The limiting values of the current correspond-

Series I.

$K = 585$ *cm.* $L = 3.01$ *henry.* $R = 62.2$ *ohm.*

	R_b	±	E	I	k	v
1	50.0	2.0	2.032	.01810	13.29	77.2
2	37.7	.2	2.032	.02032	22.08	99.6
3	27.3	.2	2.029	.02272	30.02	116.4
4	19.2	.2	2.029	.02496	40.89	135.4
5	18.5	.5	2.030	.02517	40.89	135.4
6	10.2	.2	2.030	.02806	56.01	158.8
7	75.0	5.0	2.030	.01482	6.59	54.5

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ing to the velocity of break were measured within one per cent. except where specified. The inductance and velocity of break are known to a much greater degree of accuracy. All quantities are in the usual units except the capacity, kept in cm. for convenience.

The total resistance, from which I is calculated, is $R_b + R$ plus the small resistance of the leads and break, which was found to be negligible in the above results. The accuracy of the results 2–6

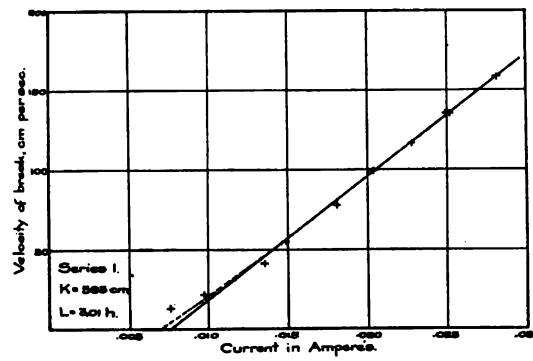

Fig. 7.

is thus seen to be well within one per cent. The currents and velocities of break are plotted as abscissæ and ordinates respectively, being all but the lowest three points of Fig. 7 which belong to the next series. It will be seen that the relation is approximately a linear one.

We may write equation (1) thus:

$$v = AI - B + \frac{C}{I}, \tag{1}$$

where C has the value $.1290b^2/aL$. For the moment let us assume for a and b the values obtained by Earhart. Taking representative value of the current, .025 am. say, the third term on the right of (1) has the value 3 cm./sec. It will differ from this by only one or two for any other value of the current in the range. The velocities run from 50 to 160 cm./sec. Accordingly the C term in the above equation is in the nature of a small correction to the equation.

$$v = AI - B, \tag{2}$$

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the asymptote of (1). Selecting the values 2–6 in the above results as being much more accurately determined than the other two, let the straight line determined by them be

(3) $$v = A'I - B'.$$

Then

$$A = 7{,}751\,; \quad B' = 58.8.$$

We have, from values of A, B and C, already given,

$$C = \frac{.1290 \times .7656}{(.8946)^2} \frac{B^2}{A}$$

Substituting the approximate values A' and B',

$$C = .055$$

The slope of the curve (3) is A' and is sensibly equal to the slope of the curve (1), especially for larger currents. We have then, for the current $I_1 = .025$ am. say,

$$A = A' + C/I_1^2 = 7{,}839,$$

which will differ by one per cent. or less if we choose any other current value in 2–6 as the basis of calculation. Similarly,

$$B = AI_1 - v_1 + C/I_1 = 63.1$$

where v_1 is taken from the curve (3) to correspond to I_1.

The curve $v = 7{,}839I - 63.1 + .055/I$ is shown deviating from the straight line to the left in Fig. 7. What we have done in getting the constants is equivalent to assuming that the curve (1) is tangent to (3) at the point (I_1, v_1). The justification lies in the fact that the curve (1) satisfies the points in the range of observation 2–6 as well as the line (3).

Since

$$A = 7{,}839 = \frac{.7656}{aK}, \quad a = 150{,}000 \text{ volts/cm.},$$

and since

$$B = 63.1 = \frac{.8496b}{a\sqrt{KL}}, \quad b = 474 \text{ volts.}$$

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The constant a comes out about double the value found by Earhart and b comes out one third greater. We shall see that this increase is clearly explained by the lag effect.

In showing the order of magnitude of the C term in (1) we used Earhart's values for a and b. If we use our own values it will come even smaller.

It is clear from this experiment that the lag effect is independent of the initial current, that is, of the magnitude of the induced potential, when the constants of the circuit are kept the same, since we get an approximately linear relation for v and I in agreement with the theory. Jaumann's hypothesis that the spark lengths for rapidly varying potential depend upon a definite value of VdV/dt is thus not borne out.

An attempt was next made to get values of v for very small initial currents. We should expect, when we approach induced potentials of the order of the minimum spark potential, to get a change in the spark constants, as in Earhart's results (Fig. 2), where, for $V < 351$ volts, we have $V = gx$, where g is about 1.2×10^6 volts /cm. For this branch of the curve the relation between the velocity of break, current, and constants of the circuit may be found by putting $b = o$ and $a = g$ in eq. (I). Then we have $v = .7656\ I/gK$. Accordingly, for smaller and smaller currents, we should at length come to an abrupt deviation from the straight line intersecting the I axis as in Fig. 7 and the points would rapidly approach the origin.

The readings for such small currents were very difficult to obtain owing both to the small readings of the electrometer, and to the minuteness of the spark, which rendered it difficult to determine whether the spark had or had not taken place. The following values were obtained:

SERIES II.

Constants as in Series I.

	R_b	±	E	I	k	v
1	205	5	2.028	.00760	.390	13.2
2	146	1	2.025	.00973	1.05	21.7
3	87	2	2.025	.01357	3.70	40.8

giving the lowest three points in Fig. 7. We have perhaps an indi-

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cation of the change in the first two points. For the first the maximum induced potential is 517 volts.

Experiments were next tried to find whether the spark constants, not affected by changes of current, would be affected by change of capacity.

SERIES III.

K = 789 *cm.* *L* = 3.01 *henries.* *R* = 62.2 *ohms.*

	Total *R*	*E*	*I*	*h*	*v*
1	101.0	2.043	.02020	9.65	65.8
2	73.0	"	.02801	30.45	116.9
3	71.5	"	.02856	31.67	119.3
4	71.2	"	.02870	34.30	124.1
5	69.0	"	.02964	38.56	131.6
6	81.2	"	.02516	21.07	97.2
7	172.6	4.093	.02372	17.10	87.6
8	154.8	4.088	.02642	24.99	106.0
9	228.8	4.085	.01786	6.41	53.7
10	197.8	"	.02066	11.79	72.8
11	165.8	"	.02464	18.49	91.2

The straight line given by (I, v) is plotted in Fig. 8, No. III.

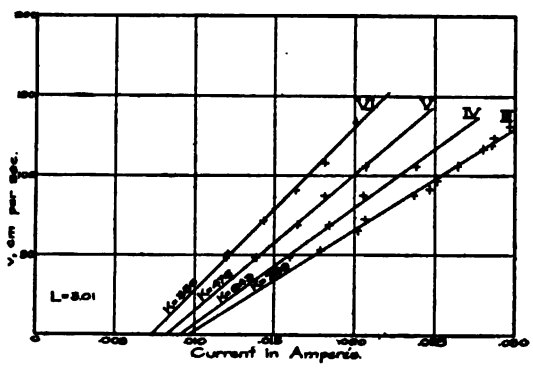

Fig. 8.

Using the same method as before for obtaining A, B, and C, we obtain

$$A = 6{,}510; \quad B = 67.9; \quad C = .074.$$

Whence $a = 134{,}100$ volts/cm.

$b = 523$ volts.

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SERIES IV. (Fig. 9, *II.*)

K=643 *cm.* *L and R as in III.*

	Total *R*	*E*	*I*	*k*	*v*
1	256.3	4.088	.01594	5.16	48.1
2	222.6	4.093	.01838	10.44	68.5
3	199.6	4.093	.02052	17.10	87.6
4	171.8	4.088	.02380	24.99	106.0

From which

$$A = 7{,}578; \quad B = 75.3; \quad C = .077.$$

and

$$a = 141{,}400 \text{ volts/cm.}$$

$$b = 552 \text{ volts.}$$

SERIES V. (Fig. 9, *III.*)

K=476 *cm.* *L and R as before.*

	Total *R*	*E*	*I*	*k*	*v*
1	294.7	4.088	.01386	5.16	48.1
2	249.6	4.093	.01641	10.44	68.5
3	225.8	4.088	.01812	17.10	87.6
4	197.8	4.088	.02066	24.99	106.0

giving

$$A = 8{,}748; \quad B = 77.7; \quad C = 0.71.$$

$$a = 165{,}500 \text{ volts/cm.}$$

$$b = 573 \text{ volts.}$$

SERIES VI. (Fig. 9, *IV.*)

K=356 *cm.* *R and L as before.*

	Total *R*	*E*	*I*	*k*	*v*
1	338.7	4.088	.01206	5.16	48.1
2	336.8	4.073	.01210	5.96	51.7
3	284.8	4.073	.01431	11.40	71.6
4	249.8	4.073	.01634	18.31	90.7
5	224.8	4.070	.01811	25.85	107.8
6	202.8	4.070	.02006	39.63	133.4

giving

$$A = 10{,}390; \quad B = 81.5; \quad C = .066.$$

and

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$$a = 186{,}200 \text{ volts/cm.}$$

$$b = 585 \text{ volts.}$$

From Fig. 9 it is seen that for diminishing capacity, the curves (I, v) progress toward the origin and increase in slope, agreeing with equation (1). But the increase in slope is not so great as would be expected, for the quantity a steadily increases, as we may see from the following summary of series I., III.–VI.

Series.	K cm.	a	b
III.	789	134,100	523
IV.	643	141,400	552
I.	585	150,000	474
V.	476	165,500	573
VI.	356	186,200	585

The quantity a and the quantity b, with one exception, are seen to increase with diminishing capacity. Without, for the present, considering the cause, we pass to experiments in which the capacity was kept constant while the inductance was changed.

Series VII.

$K = 789$ *cm.* $L = 1.97$ *henries.* $R = 50.9$ *ohms.*

	Total R	E	I	h	v
1	188.9	4.073	.02159	6.62	54.6
2	156.9	"	.02600	13.41	77.7
3	128.9	"	.03164	27.42	111.0
4	186.9	4.079	.02184	6.12	52.4
5	159.0	"	.02570	12.95	76.3
6	136.9	"	.02982	22.97	101.6

From these

$$A = 5{,}967\,; \quad B = 81.1\,; \quad C = .113,$$

giving

$$a = 146{,}300 \text{ volts/cm.}$$

$$b = 551 \text{ volts.}$$

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SERIES VIII.

$K = 789$ *cm.* $L = 1.32$ *henries.* $R = 38.9$ *ohms.*

	Total R	E	I	h	v
1	150	4.073	.02721	6.69	54.8
2	119	"	.03430	16.50	86.2
3	105	"	.03888	26.60	109.2
4	128	"	.03188	11.01	70.4

From which

$$A = 4{,}845; \quad B = 84.6; \quad C = .152,$$

giving

$$a = 180{,}200 \text{ volt/cm.}$$
$$b = 580 \text{ volts.}$$

These two series with III., in which the capacity was the same, are shown in Fig. 9. We notice progression away from the origin

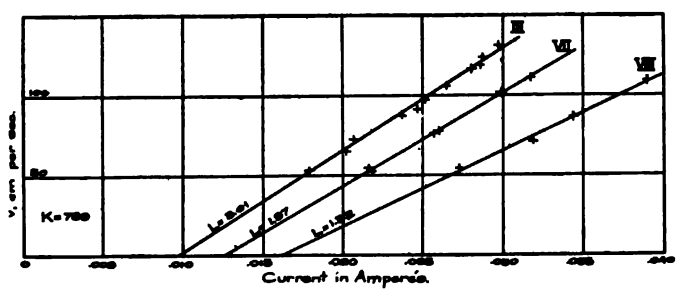

Fig. 9.

with diminishing inductance, as we should expect from the theory. But, instead of the slope being practically constant, it diminishes with the inductance. We show the results together for change of inductance.

$K = 789$ *cm.*

Series.	L	a	b
III.	3.01	134,100	523
VII.	1.97	146,300	551
VIII.	1.32	180,200	580

We notice increase of both quantities a and b with diminishing inductance, as with diminishing capacity.

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We close with one more series, in which the period is less than that in any previous set.

Series IX.

$K = 356cm.$ $L = 1.97$ *henries.* $R = 50.9$ *ohms.*

	Total R	E	I	h	v
1	216	4.079	.01882	13.50	77.9
2	189	"	.02161	23.98	103.8
3	171	"	.02390	34.98	125.3
4	203	"	.02014	17.91	89.7

giving

$$A = 9{,}550; \quad B = 108.3; \quad C = .125.$$

$$a = 202{,}700 \text{ volt/cm.}$$

$$b = 685 \text{ volt.}$$

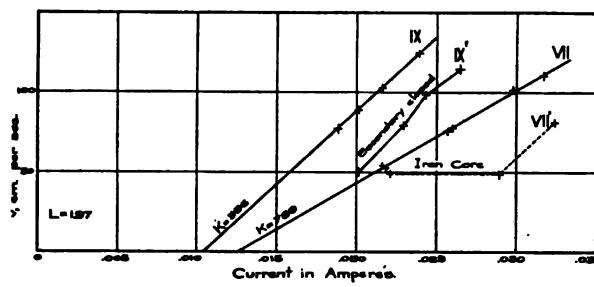

Fig. 10.

These points, with which those of series VII., are plotted in Fig. 10 for purposes of comparison.

Discussion of Results.

It might appear at first sight that the unknown capacity of the coil would explain the variation of the quantities a and b from the accepted values. If we assume $a = 70{,}000$ volt/cm. and calculate from the constants A and the capacities made necessary by the assumption, we shall find that they are all the way from two to three times the capacity which was measured. Moreover, the excess of apparent capacity over the measured capacity in series I.–VI. will be found to diminish as the latter diminishes, which is contrary to what we should expect if we were to attribute the

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apparent excess to the coil. Again, in the preliminary experiment, no perceptible difference was noticed, whether the battery side of the circuit was or was not earthed. We may therefore assume that the whole of the coil is at practically a node of potential and that its capacity is negligible.

We may very simply explain the results on the basis of any theory which takes into account the fact that an appreciable time must elapse after the application of a potential to a spark gap before a spark can take place, some process going on which converts the gas between the electrodes from an insulator into a conductor.

Such a theory has been developed by J. J. Thomson.[1] He obtains for the equation for the production of ions by an electric field between two parallel plates

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial x}(nu) = \frac{nu}{\lambda}\{f(Xe\lambda) - \gamma\}.$$

where n is the number of ions per cubic centimeter, X is the electric force u, λ, e, and $Xe\lambda$ are respectively the average velocity, mean free path, charge and mean kinetic energy of an ion. γ is a constant.

The complete solution of the above equation for n will be an exponential function of the time. The density of ionization and, accordingly, the conductivity of the gas will increase in geometric progression until they reach the required value for sparking, when $\partial n/\partial t$ becomes zero. With the electric force and spark length kept constant, the condition that the gas has reached the steady state, gives for the spark potential, according to J. J. Thomson,

$$V = ad + b,$$

for spark lengths, d, greater than the critical spark length, a and b being constants.

For the purposes of this paper we require the solution of the differential equation for the following condition: Given a spark length d, what will be the potential necessary to produce a spark at the time t? It seems probable that it will be of the form

[1] J. J. Thomson, Phil. Mag. (5), 50, p. 278, 1900. See also Conduction of Electricity through Gases, pp. 231, 341, 379.

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$$V = (a + m)d + b + n.$$

When m and n are such functions of the time that when t approaches zero they become indefinitely large and, conversely, when t becomes large they will become zero and V will have its normal value. m and n are thus measures of the lag effect.

Although we have V and x, the spark length, as functions of the time, we may show that the conditions of our experiments are such that the electric force will be only dependent upon the time to the second order. This will be evident without proof if we consider that the conditions are such that the limiting condition for sparking requires that the induced potential and the spark gap increase at roughly the same rate. The problem is thus reduced approximately to the one stated above.

We may show also that the electric force, under the experimental conditions, is such as to be independent of the current for larger values of the latter, for we found by experiment that $v = AI - B + C/I$. The spark length is proportional to v. The electric force, then, will contain I only in the denominators of the small terms. This gives us justification for calculating a and b from A and B of the previous series, for that calculation involves the assumption that the lag effect is constant for a given period regardless of the initial current.

The constants m and n will depend upon the time at which the spark takes place. This time, as given in the first part of this paper is

$$t = \sqrt{KL}\cos^{-1}\left(\frac{a'vK}{I}\right) = \sqrt{KL}\left(\frac{\pi}{2} - \frac{a'vK}{I}\cdots\right)$$

where $a' = a + m$. We have seen that $a'vK/I$ is small in the limits of our experiment, being from .2 to .4. We may therefore consider the time required to be roughly proportional to the period, and for purposes of illustration we may take m and n as such functions of the period that they will vanish when the latter is infinitely large, and become themselves infinite when the period approaches zero. This will be true in general for m at least, whatever theory of ionization we adopt. The simplest functions which will satisfy the relation will be

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$$a' = a + m = a\,(1 + \alpha/\sqrt{KL})$$
$$b' = b + m = b\,(1 + \beta/\sqrt{KL})$$

where a' and b' are the quantities previously called a and b in the tables, and α and β may be considered as time constants of the gas.

The following results from series I.–IX., with the preliminary experiment P, show the dependence of a' and b' upon the period. Three significant figures are kept.

Series.	$\sqrt{KL} \times 10^5$.	$t \times 10^5$.	a'	b'
IX.	2.79	3.30	203,000	685
VIII.	3.40	3.88	180,000	580
VI.	3.45	3.86	186,000	585
V.	3.99	4.52	165,000	573
VII.	4.16	4.82	146,000	551
I.	4.42	4.59	150,000	474
IV.	4.64	5.43	141,000	552
III.	5.14	5.76	134,000	523
P.	8.05	10.14	93,000	

The time t is calculated from the formula just given, using the mean value of $a'vk/I$ in series I.–IX., and in the preliminary ex-

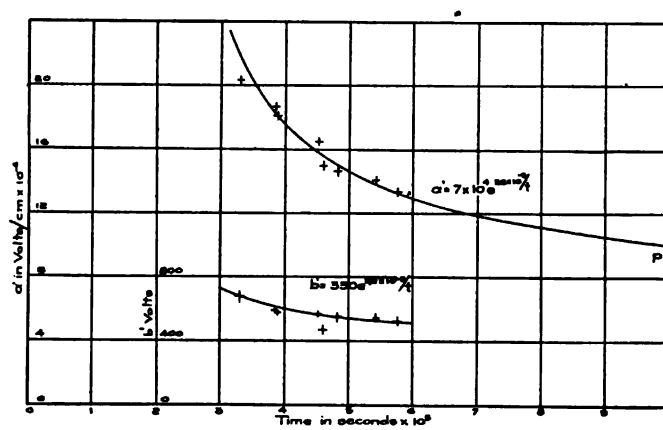

Fig. 11.

periment using the mean value of K. The plots of a' and b' with the times as abscissæ are shown in Fig. 11.

The function $a' = a(1 + \alpha/t)$ seems to satisfy the results of series I.–IX. as well as any function which could be chosen. But it

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comes very wide of the point P, obtained from the preliminary experiment, which, while given no weight in the calculations, is supposed to be determined within five per cent. The spark constant a, calculated from the results will be about 5×10^4 volt/cm. in place of Earhart's value of about 7×10^4. Though our data are not sufficiently extensive to enable us to tell definitely, it would seem that the function m must be some function of the time which diminishes more rapidly as the time increases than does aa/t.

If we put $a' = ae^{\alpha/t}$, and assume $a = 70{,}000$ volts/cm., the mean value of α from the nine series is 3.6×10^{-5} sec. The curve thus obtained is the upper one in Fig. 11. It gives a value within 8 per cent. of the a' given by the preliminary experiment.

The curve obtained through the observations b' is obtained by putting $b = 350$ volts and $\beta = 2.2 \times 10^{-5}$ sec. in the equation $b' = be^{B/t}$.

Addenda.

Though the aim of the work here described was to study the conditions for sparking at the break of the primary circuit, some experiments were made with the view of finding what the condition would be for the primary of the induction coil with iron core and with closed secondary. The presence of an open secondary was found to be without perceptible effect on the necessary velocity of break for a primary circuit.

Secondary Closed. — In Series IX. the inductance used consisted of the first five parts of the coil described by Dr. J. E. Ives,[1] the sixth part being disconnected and open. When the latter was closed a falling off was found in the necessary velocity of break for given current. This is shown by the crooked line under IX. in Fig. 10. This is due to the absorption of energy by the secondary as was shown by the diminished electrometer readings for the primary oscillations.

When the secondary was connected to an electrometer and readings taken simultaneously with those of the primary electrometer, the maxima of electrometer readings for the two circuits were found to occur at the same time; *i. e.*, the induced potential in the secondary is a maximum, when the current in the primary has its greatest

[1] Loc. cit.

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possible value consistent with no sparking at the break. This is equivalent to the well known fact that the secondary potential is greatest when the optimum capacity is used with the primary. Moreover, it was found that the greater the velocity of break the greater the possible secondary potential, because it enables the primary current to be made larger, or the capacity to be made less. This is in direct agreement with Lord Rayleigh's result.

Core. — Heavy cores of brass were used without perceptible effect on the necessary velocity of break. After Series VII. was obtained, bundles of iron wire were introduced into the core of the coil, and caused a marked falling off of the necessary velocity of break, as shown by the dotted line in Fig. 10. There was also a great falling off in the electrometer readings, probably due to the hysteresis loss and the lengthening of the period. According to a principle laid down by B. Walter[1] "the maximum potential for the secondary, excepting for losses of electric energy through break sparks, magnetic and dielectric hysteresis, and Joule's heat, is directly proportional to the maximum value of the potential of the primary." When the secondary is open, the velocity of break necessary to prevent sparking will be determined by the constants of the primary circuit and by the value of the initial current; and this velocity of break will permit of the highest possible secondary potential. When the secondary is closed, energy is absorbed from the primary, the necessary velocity of break will be less than for open secondary. The investigation will be complicated in this case by the introduction of a damping factor in the primary circuit.

Mercury Break. — In some early experiments a study of the mercury break was made. The break consisted of a blunt needle which was withdrawn at a definite rate from a well of mercury. Photographs were taken of the break, the illumination being that of its own spark. It was found that a column of mercury followed the needle for a short distance above the surface before separation took place. The velocity of break is thus not as great as could be obtained with a mechanical break going at the same rate, showing the decided advantage of the latter. No dependence of optimum capacity and velocity of break could be found except for very small

[1] B. Walter, Wied. Ann., 62, p. 300, 1897.

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induced potentials. This we should expect, since a given point has a fixed discharge potential such that for higher values discharge will occur independently of the distance.

It was found that the capacity necessary to prevent a spark at the break was about one half as much when the needle was connected to the positive pole of the battery as was required when it was connected to the negative pole, so that much greater induced potentials could be reached in the former case than in the latter. This agrees with results which have been published by Dr. J. E. Ives.[1] It is probably due to the fact that the discharge potential for a negatively electrified point is less than for the same point positively electrified[2] and is a good point to be remembered by those using the mercury break with an induction coil.

Summary.

This work was undertaken in the hope of finding relations which were indicated in some experiments by Lord Rayleigh, existing between the constants of an oscillatory electric circuit, such as the primary of an induction coil, the initial current, and the velocity with which the contacts of the break are separated, when the conditions are just sufficient to prevent sparking at the break.

By neglecting the "lag" effect in the spark, a theoretical relation was found, and may be roughly expressed by saying that the velocity of break necessary to prevent a spark will be proportional to the frequency of oscillation and a linear function of the maximum induced potential, the latter implying a linear relation between velocity of break and initial current.

The necessary velocity of break was found experimentally to be:

1. A linear function of the initial current (see Figs. 7–10).

2. For given current, increasing in value in a manner consistent with the equation when the capacity is diminished (Figs. 6, 8, 10).

3. Diminishing according to the equation when the inductance is diminished (Fig. 9.)

The assumption that the lag of the spark might be neglected did not hold true. It was found that the spark constants, a and b,

[1] J. E. Ives, On the Asymmetry of the Mercury Break, Phys. Rev., 17, p. 175, 1903.
[2] Tamm, Annalen der Physik, 6, p. 259, 1901.

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were too large, but diminished systematically as the time between the application of the potential and the passage of the spark increased, and would apparently reduce to the ordinarily accepted values if the time were great enough to allow the gas to become sufficiently ionized.

The results enable us to place a limit on the velocity of break necessary to prevent a spark at the break of an inductive circuit, if we know the inductance, capacity and initial current. The necessary velocity will be lessened by any condition which causes the absorption of energy from the primary, such as a closed secondary, hysteresis, heat losses, etc.

The method here developed seems to be well adapted to the study of the lag effect in the electric spark, or of the ionization produced by an electric field. A method in which use is made of constant potentials is likely to present great mechanical difficulties, especially as these results seem to show that the potential necessary to produce a spark across a given distance within the time t will have decreased from infinity to only e times its normal value in about 3.6×10^{-5} sec. The mechanical difficulties are reduced to a minimum in the present method, the main trouble to be expected lying in the interpretation of results. I hope soon to carry out similar experiments with the method much improved and with results covering a wider range for the purpose of getting data on the ionization produced by an electric field.

I wish to express my best thanks to Professor Arthur G. Webster, who has constantly aided me with suggestions, and to the authorities of Clark University for the facilities placed at my disposal.

July, 1904.

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EXPERIMENTS ON RESONANCE IN WIRELESS TELEGRAPH CIRCUITS. PART IV.

By George W. Pierce.

X. The Direct Coupled Type of Sending Circuit.

In the previous parts[1] of this research an account was given of experiments on the resonance conditions in wireless telegraph circuits of the "electromagnetically-connected" type. It is proposed in the present paper to present the results of similar investigations with other types of circuits.

The sending station in the set of experiments here described was kept constant throughout, and is represented diagrammatically in Fig. 30. It is seen to consist of an autotransformer instead of the tesla arrangement of the previous experiments. The high frequency oscillations in the sending antenna are produced by the discharge of a condenser through some of the turns of an inductance in the mast circuit.

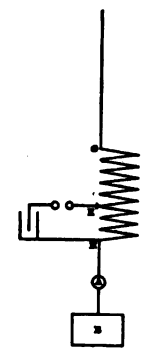

Fig. 30.

This form of sending circuit is employed in several of the commercial systems of wireless telegraphy at present in operation. Itseems to have been first proposed by Professor Ferdinand Braun of Strassburg, and is covered by German Patent No. 111,578, issued October 14, 1898, to the Gesellschaft für drahtlose Telegraphie. Braun's claim of priority in the use of this circuit is substantiated by Righi and Dessau,[2] Max Wien,[3] Fleming and various other writers on wireless telegraphy. For example, Fleming[4] says, "The second method, due to Braun, consists of attaching the aerial to some point on an oscillation circuit consisting of a condenser, an

[1] Physical Review, Vol. XIX., p. 196, 1904; Vol. XX., p. 220, and Vol. XXI., p. 367, 1905.

[2] Righi and Dessau, Telegraphie Ohne Draht, p. 416, 1903.

[3] Wien, Ann. d. Phys., 8, p. 686, 1902.

[4] Fleming, Pop. Sci. Monthly, June, 1903.

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inductance coil and a spark gap, in series with one another, and charging and discharging the condenser across the spark gap so as to create alternations of potential at some point on the oscillation circuit. The length of the aerial must then be so proportioned * * * that it is resonant to this frequency."

Adjustment of Sending Circuit. — Evidently in order to produce a strong radiation of electric waves the different parts of the sending station must be properly proportioned. This adjustment may be made in several ways; by variation of the capacity of antenna, the capacity of the condenser, the whole inductance *GH*, or the part of the inductance in the condenser circuit *KH*.

For the present experiments the first three of these quantities were arbitrarily chosen and kept constant, and adjustment was made by moving the connector *K* to various points on the inductance. At each position the key in the primary of the charging transformer was closed and the current between the antenna and the ground was read on a hot-wire ammeter at *A*. The connector *K* was finally set at the position that gave the greatest current in the ammeter. This adjustment makes the sending station into a system with a strong oscillation of current in the antenna, which is the condition for a strong radiation of energy.

The dimensions of the parts of the sending station in their final adjustment had the following values:

The sending antenna, shown in Fig. 13 of Part II., extended to a height of 15.8 meters above the mast inductance. For the greater part of its length it consisted of four wires .208 cm. in diameter and 59 cm. apart.

The coil *GH*, Fig. 30, consisted of five turns of wire .208 cm. in diameter wound in a spiral 46 cm. in diameter with a pitch of 5.08 cm. The total inductance of this coil, measured on a Rayleigh's bridge, is 1.56×10^{-5} henries.

The part of the coil between the leads to the condenser, *KH*, consisted of 1.2 turns and had an inductance of $.151 \times 10^{-5}$ henries.

The condenser was made up of sheets of copper separated by miconite plates. Its capacity was not measured.

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XI. Resonance Curves with the Direct Coupled Sending Station and Various Forms of Receiving Circuit.

Experiment XII. Tuning the Receiving Circuit with a Variable Inductance in the Antenna. — In many of the wireless telegraph plants in commercial operation the receiving station is tuned by varying an inductance placed above the instrument in series with the antenna. This is the method of the present experiment. Fig. 31 is a diagram of the receiving circuit. The receiving instrument represented at I is the high frequency dynamometer used in the previous experiments. The coil of the dynamometer has a resistance of 1.33 ohms and an inductance of 1.17×10^{-5} henries.

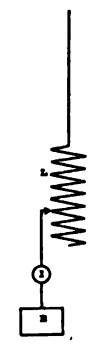

Fig. 31.

The tuning coil L is a variable inductance and consists of 51 turns of copper wire .208 cm. in diameter, wound on a vulcanite drum 13 cm. in diameter. The pitch of the windings is .42 cm. Variation of its inductance is made by a wheel contact moving along the wire as the drum is rotated. Values of the inductance for various positions of the movable contact are known from a calibration of the tuning coil by the aid of a Rayleigh's bridge. The inductance of the whole of the tuning coil is 16.5×10^{-5} henries. Any fraction of this inductance can be used.

The experiment consists in finding what inductance is required to be added by the tuning coil L in order to bring the receiving station to resonance with the sending station when various lengths of antenna are used at the receiving station. Quantitative readings were taken so as to give also the shape of the resonance curves and the intensity of the signals received.

A set of observations with this method of tuning are shown in the curves of Fig. 32. The different curves were obtained with different heights of the receiving antenna, the heights being designated by the numbers at the vertices of the curves. The abscissas of the curves are the inductance of the tuning coil; the ordinates are the deflections in centimeters all reduced to one scale, namely, the deflection that would be had if the receiving instrument should be set at one fiftieth its best sensitiveness.

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Each curve has two distinct maxima, showing that the direct coupled sending circuit like the electromagnetically coupled circuit has two distinct periods of oscillation, as has been frequently pointed out.

Sharpness of Resonance. — The curves of Fig. 32 are seen to be very obtuse in comparison with those obtained with the arrangement of apparatus in the previous papers. For example, the first curve of the present series has a maximum for 1.8×10^{-5} henries of added inductance, which together with the inductance of the instrument makes the total inductance 2.97×10^{-5}. The deflection drops to half for a decrease of 26 per cent. or an increase of 60 per cent. of this value. This result compares very unfavorably with

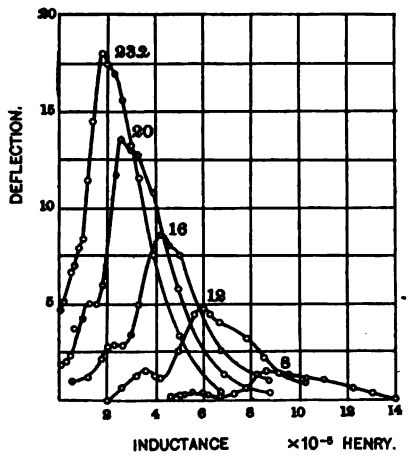

Fig. 32.

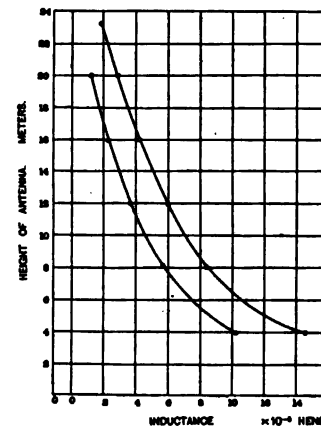

Fig. 33.

some of the curves of the previous research with the electro-magnetically coupled system, where a corresponding change of 5 per cent. or even 2.5 per cent. has caused the energy received to drop to one half. This loss in sharpness of resonance does not seem to be adequately compensated for by a gain in intensity of signals, for the deflections in the present experiment are only 1.4 times as great as those that were obtained in the case that gave the fall of energy to one half for a 5 per cent. departure from resonance. The power expended at the sending station was about the same in the two cases.

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Relation Between Height of Antenna and Resonant Inductance in the Tuning Coil. — As the length of antenna is diminished in the above experiment, the inductance in the mast circuit must be increased in order to obtain maximum deflection with a fixed frequency of incident waves.

TABLE XIV.

Showing Inductance Required for Resonance. Height Varied. Incident Waves Constant.

Height, Meters	L' Henry.	L'' Henry.	l' Meters.	l'' Meters.
23.2	1.8×10^{-5}		4.08	
20	2.65	1.2×10^{-5}	5.30	2.86
16	4.2	2.35	7.35	5.30
12	5.0	3.6	9.60	6.50
8	8.5	5.6	12.25	9.00
4	14.6	10.3	18.80	14.30

Table XIV., taken from the curves of Fig. 32, shows the values of the inductance of the tuning coil required with various heights of antenna in order to obtain the maximum deflection. L' is the inductance that produces the strong maximum, and L'' the weaker maximum; l' and l'' are the length of wire in these two inductances respectively. The two maxima arise in the existence of two periods of the incident waves.

The values of L' and L'', recorded in Table XIV., are plotted in Fig. 33, in which the two curves relate to the two periods. These are empirical curves. The distance OO' is the inductance of the instrument. The fact that the curves of Fig. 33 are not straight lines shows that the problem of the propagation of electric waves in wire wound in a coil is less simple than the problem of its propagation in a straight wire. In the case of the non-magnetic straight wire in air the self inductance per unit of length is inversely proportional to the capacity per unit length, so that the velocity of propagation in the wire, as derived from the wave equation, is constant and is equal to the velocity of light. This deduction from the theory of electric waves has been amply verified by experiments. In some other simple cases, *e. g.*, the case of two parallel wires or two coaxial cylinders, the same relation of inductance to capacity holds and the velocity of the waves in such conductors is the velocity of light. On the other hand, in the case of the solenoid here

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used as a tuning coil, in order to give curves of the shape of those of Fig. 33, the velocity of the waves is different from the velocity of light and furthermore the velocity of the waves in the solenoid is different in different parts of the solenoid. This is evident if we recall that with a resonant receiving circuit the time for the wave to travel from the top of the receiving antenna to the ground is one fourth the period of the sending circuit. When we shorten this time by cutting off antenna we must increase it equally by adding inductance if the circuit is to remain resonant.

It is seen from the curves that for *equal* decrements of the length of antenna, which are proportional to decrements in time, we need to make *unequal* increments of the inductance, which are, therefore, not proportional to the time. In a similar way, by plotting length of antenna against length of wire in the solenoid (curves not here given), it may be seen that lengths on the solenoid are not proportional to the time for waves to traverse them ; that is the velocity of the waves on the wire of one part of the solenoid is different from their velocity on the wire of another part of the solenoid. In terms of the theory of electric waves in a conductor this is equivalent to saying that the inductance per unit of length of the solenoid is not inversely proportional to the capacity per unit of length of solenoid. This same result has been reached by Drude,[1] in a masterly theoretical and experimental research on the natural period of electric oscillation of solenoids with antenna attached.

The wave-length here used is determined in the next experiment in which the conditions prove to be simpler.

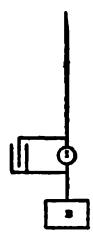

Fig. 34.

Experiment XIII. Tuning the Receiving Circuit by a Variable Capacity Shunted About the Instrument. — The form of receving circuit employed in this experiment is shown in Fig. 34. When the antenna has not sufficient capacity to be in resonance with the incident waves, additional capacity is introduced in the form of a variable condenser shunted about the coil of the receiving instrument. The condenser used is one of the calibrated air condensers described in Part I.

Evidently as the length of antenna (a single wire .208 cm. in diameter) is diminished, the shunted capacity must be increased. A

[1] Drude, Ann. der Phys., 9, p. 293, 1902, and 11, p. 957, 1903.

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set of the observations obtained is presented in the curves of Figs. 35 and 36. (In order to bring out details the curves of Fig. 36 have their ordinates magnified[1] twenty-five times with reference to Fig. 35.) The numbers at the vertices of the curves designate

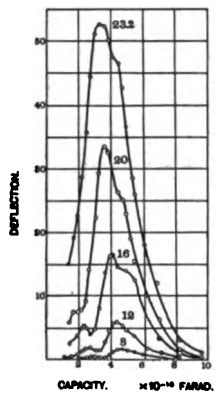

Fig. 35.

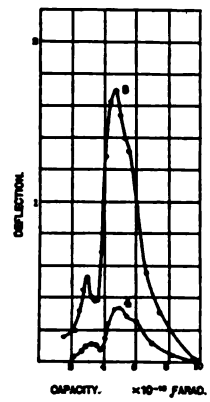

Fig. 36.

heights of antenna in meters. The abscissas are capacity of shunt, and the ordinates are the deflections, reduced to centimeters at one fiftieth the best sensitiveness of the receiving instrument.

These curves bear a marked resemblance in form to the curves of Fig. 32. The irregularities near the summits, possessed in common by the two sets of curves, evidently belong to the wave produced at the sending station and are not characteristic of the receiving station.

Other experiments have shown that these irregularities may be eliminated by better adjustment of the parts of the sending circuit to resonance with each other.

Sharpness of Resonance. Hysteresis Loss in Dielectrics Other Than Air. — As to sharpness of resonance the curves obtained by tuning with the aid of the shunted capacity are about equivalent to those obtained by tuning with inductance in series. It might be remarked in passing that glass condensers and mica condensers, when used in place of the air condenser at the receiving station, gave about the same sharpness of resonance and nearly the same intensity of signals as the air condensers.

[1] Small readings are made with as great accuracy as large readings, because the small readings are taken as large deflections with increased sensitiveness of the instrument.

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To show the relative merit of the two dielectrics the following readings of deflections, Table XV., are taken at random from among the observations in which both glass and air condensers were used as shunts about the receiving instrument.

TABLE XV.

Showing Relative Merit of Glass and Air as Dielectrics.

	Air.	Glass.	Glass / Air.
Deflection.	7.0	6.6	.95
	8.6	7.9	.94
	11.3	10.6	.95
	39.0	37.7	.97
	54.0	49.5	.91
			Mean .94

Whence it is seen that in comparison with air the loss of energy by hysteresis or leakage when glass is used as dielectric in the condenser at the receiving station amounts to about six per cent.

Experiments were also made with mica and waxed silk as dielectrics, but the comparison with the air condensers in those cases were not direct, so the numerical data are not reported. It appeared, however, that with the present form of receiving circuit Fig. 34, condensers of either of these substances or of glass may be used in place of air condensers at the receiving station without great loss of energy. An exhaustive study has not yet been made with a variety of dielectrics, and the result here given should be regarded merely in the nature of a preliminary note.

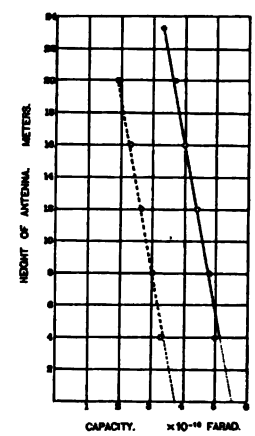

Fig. 37.

Relation between the Length of Antenna and the Resonant Capacity of the Condenser Shunt. — In Fig. 37, height of antenna is plotted against the shunt capacity required for resonance. The relation is more simple than the relation of resonant inductance to height in the previous experiment, and is represented by two straight lines, corresponding respectively to the two periods of the incident waves.

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The straight line relation is taken to indicate that as capacity is cut off from the antenna equal capacity must be added in the condenser about the instrument. If we proceed on this theory it is easy to determine the two wave-lengths sent out from the sending station.

The straight lines in Fig. 37, when produced, cut the axis of abscissas at the points $C' = 5.5 \times 10^{-10}$ and $C'' = 3.7 \times 10^{-10}$ farads. These quantities give respectively the values of capacity that shunted about the instrument *with zero antenna attached* form the two cases of closed circuits in unison with the sending station. The period of such closed circuits is given by the formula

$$T = 2\pi\sqrt{LC}. \tag{1}$$

Knowing L, the inductance of the instrument, and the two values of C (C' and C'') we may obtain the two periods of the sending circuit by substituting these quantities in equation (1).

$$T' = 2\pi\sqrt{5.5 \times 1.17 \times 10^{-15}} = 51 \times 10^{-8} \text{ sec.},$$

and

$$T'' = 2\pi\sqrt{3.7 \times 1.17 \times 10^{-15}} = 43 \times 10^{-8} \text{ sec.}$$

Whence the two wave-lengths of the sending system are

$$\lambda' = vT' = 153 \text{ meters}, \quad \text{and} \quad \lambda'' = vT'' = 129 \text{ meters}.$$

Special Case of the Electromagnetically-connected Receiving Circuit. — The straight-line relation shown in Fig. 37 may be derived theoretically by treating the circuit with capacity shunted about the receiving instrument, Fig. 34, as a special case of the electromagnetically-connected receiving circuit given in Fig. 10, Part II. In Part II. (cf. eq. (4), p. 246, Vol. XX.) it is shown experimentally and theoretically that the condition for resonance is

$$(L_3L_4 - M^2)\omega^4 - \left(\frac{L_3}{C_4} + \frac{L_4}{C_3}\right)\omega^2 + \frac{1}{C_3C_4} = 0. \tag{2}$$

With the arrangement of apparatus in the present experiment

$$L_3 = L_4 = M.$$

Whence, the condition for resonance becomes

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$$\omega^2\left(\frac{L_3}{C_4}+\frac{L_3}{C_3}\right)=\frac{1}{C_3C_4} \tag{3}$$

or

$$C_3+C_4=\frac{1}{L_3\omega^2} \tag{4}$$

In this equation C_3 is the capacity of the receiving antenna and is approximately proportional to its length; C_4, the capacity of the condenser shunted about the instrument; L_3, the inductance of the instrument; and ω the angular velocity of the incident waves. Equation (4) is the linear relation shown in Fig. 37 and discussed in the preceding section.

If we let $C_3 = 0$, and make use of the corresponding values of C_4, we obtain equation (1) and confirm the above calculation of wave-lengths.

This remark is here inserted as an example of the manner in which the whole theory of the direct-coupled system of wireless telegraphy may be regarded as a special case of the electromagnetically-connected system studied in Parts I., II. and III. of this research.

Capacity of Receiving Antenna. — In Fig. 37 the linear relation between the height of antenna and the capacity that must be shunted about the instrument to produce resonance gives a simple method of obtaining approximately the capacity of a given length of the antenna. For example, the right hand straight line shows that 23.2 meters of a single wire .208 cm. in diameter with an added condenser capacity of 3.4×10^{-10} farads gives the same period of oscillation as 4 meters of wire with an added capacity of 5.0×10^{-10} farads. That is, when we cut off 19.2 meters of antenna, we must add 1.6×10^{-10} farads as a compensation, and if we neglect the fact that the capacity of the wire is distributed instead of localized, we may say that 19.2 meters of this particular wire has a capacity of 1.6×10^{-10} farads. This would give the value 8.35×10^{-12} farads as the average capacity of one meter of the antenna, a value that agrees satisfactorily with the value 8.2×10^{-12} computed from the usual formula for the capacity per unit length of a straight conductor

$$K=\frac{l}{2\ln l/r},$$

in which r is the radius of the wire in centimeters, $l = 100$ cm., and ln means natural logarithm.

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The parallelism of the two straight lines of Fig. 37 arises in the fact that both lines must give the same value for the capacity of a given length of antenna.

Relation of Integral Current Received to Height of Receiving Antenna as Determined by Experiments XII. and XIII. — As the height of the receiving antenna is diminished the amount of energy received falls off rapidly. The curves of Fig. 38 give the deflection plotted against height of antenna. The values on the lower curve *A* were obtained when the receiving circuit is brought to resonance by putting proper inductance in the mast circuit. The values on the upper curve *B* are the corresponding deflections when the receiving circuit is tuned by the capacity in shunt. All the deflections are on the same scale and were taken as alternate readings so as to eliminate uncertainties arising from any slow changes that might occur in the sending station. It is seen that the latter method of tuning gives larger deflections. The amount of the advantage the shunt capacity has over the tuning coil is different for different heights. The advantage increases with increasing height, and in the particular case studied, when the height of antenna is 23.2 meters, the deflections with the capacity in shunt are three times as great as the deflections with the tuning coil in series.

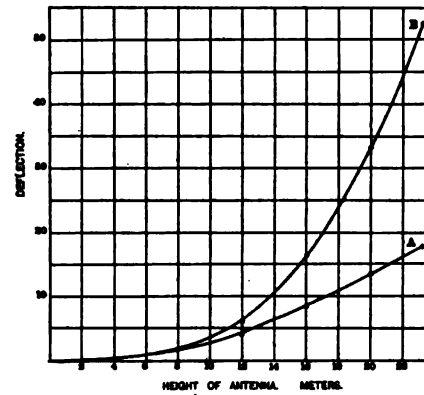

Fig. 38.

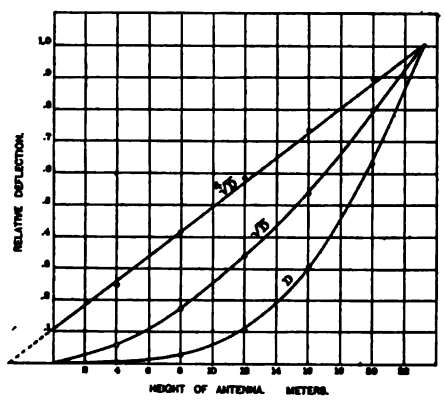

Fig. 39.

In order to examine further the relation of height of antenna to

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current in the receiving instrument the curve *B* of Fig. 38 is plotted in Fig. 39 with the ordinates all changed by a constant multiplier chosen to make the largest deflection unity. Together with this the square roots and the fourth roots of the deflections are also plotted against height of antenna. It is seen that the relation of the fourth root of the deflections to the height of antenna is represented approximately by a straight line, which cuts the axis of ordinates at 2.75 meters. The heights are here measured from the coil of the receiving instrument. If the straight line relation permits of slight extension, the negative intercept 2.75 should indicate the height of the instrument above the point of effective ground. This interpretation seems not unlikely when we take into account the fact that the wire lead from the instrument to the surface of the earth is about two meters long; this two meters is also exposed to the waves.

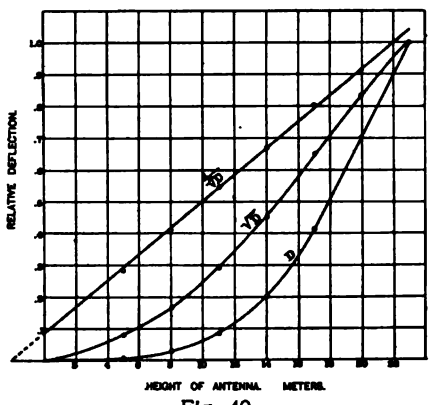

Fig. 40.

A search among earlier data in the observer's notebook disclosed that a previous experiment under different conditions, but with the same method of tuning, gives confirmatory data, which are plotted in Fig. 40 and which show also the fourth root of the deflections proportional to height. The intercept two meters in Fig. 40 is slightly less than that of Fig. 39, but the difference is not much greater than the error in determining the intercepts by lines drawn through the points.

In Part II. it was deduced theoretically and proved experimentally that the deflections of the instrument are proportional to the square of the current through it; therefore, the relation given by the curves of Fig. 39 and Fig. 40 may be stated as follows:

I. *With a constant sending circuit and a constant source of waves the current received in a circuit of the form of Fig. 34, brought to resonance by a capacity in shunt, is proportional to the square of the height of the receiving antenna measured from the "effective ground."*

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In applying this law the point of effective ground may be determined graphically if the current received from *two* heights is known. As an approximation the effective ground may be taken as coincident with the surface of the earth.

The law applies only to an approximately vertical receiving antenna, and to the capacity-shunt method of tuning. Its application to that case seems rational, because the current through the instrument is proportional to the impressed electromotive force and to the capacity of the antenna; both the capacity of attenna and electromotive force are proportional to the height of antenna: therefore, current is proportional to the square of the height of antenna.

When the series inductance is used in tuning, a different relation is obtained. The relative deflections in this case, taken from curve *A*, Fig. 38, and plotted with the largest deflection put equal to unity, are shown in Fig. 41. In this figure the square roots and fourth roots of the deflections are also plotted against height of antenna. Instead of the fourth roots of the deflections falling on a straight line as they did in the previous case, the square roots with this method of tuning are approximately in linear relation to the heights of antenna. That is

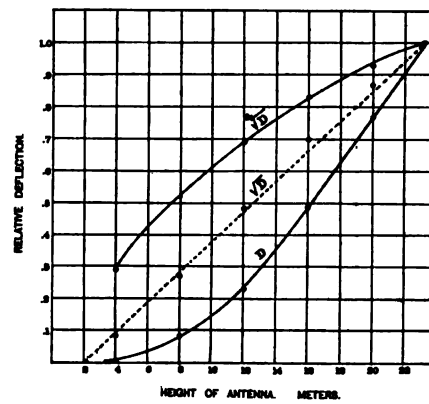

Fig. 41.

II. *The current in the receiving instrument is proportional to the height of antenna*, when the circuit is brought to resonance by added inductance in series with the antenna.

This statement is probably only an approximation, as seen from the fact that the points obtained as square roots of the deflections, instead of lying well on the dotted straight line in Fig. 41, apparently follow a wavy line about it. Also the dotted line cuts the x-axis at 2 meters, so that in applying the rule, 2 meters must be subtracted from the height of antenna measured from the receiving instrument.

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The relations I. and II. here stated for the dependence of the current in receiving instrument upon height of receiving antenna may fail of verification when tested with greater height [1] of antenna, but the results are interesting in that they show entirely different laws for the two methods of tuning.

Experiment XIV. Tuning with the Instrument in a Direct Coupled Side Circuit at the Receiving Station. — Measurements were made with the form of receiving circuit shown in Fig. 42. The points M and D are contacts movable along the tuning coil used in Experiment XIII. The inductance between M and B is referred to as the inductance in the mast circuit. The inductance in the part of the coil between D and B is the added inductance in the instrument circuit. The results obtained are shown in the curves of Fig. 43.

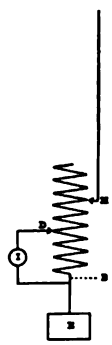

Fig. 42.

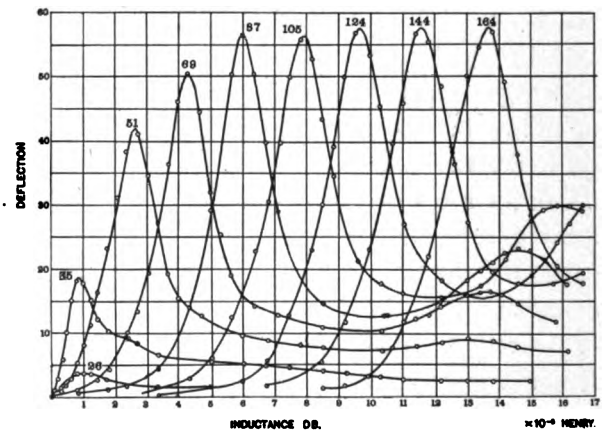

Fig. 43.

In taking any one of the curves the position of M was kept fixed at the values written at the vertices of the curves, which when multiplied by 10^{-6} give the inductance in the mast circuit. Deflections were then taken for various positions of the contact D, that is for various values of the inductance in the instrument circuit.

The height of the receiving antenna, 23.2 meters, remained unchanged during the experiment.

[1] In the experiments the height of antenna extended from 4 meters to 23.2 meters, that is to a little more than half of the quarter wave-length.

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The meaning of the curves of Fig. 43 is made clear by a reference to Fig. 44, in which inductance in the mast circuit is plotted against the total inductance required in the instrument circuit to produce resonance. The former values are the numbers written at the vertices of the curves; the latter are the ordinates belonging to those respective vertices plus the inductance of the instrument.

Fig. 44 is a straight line and the corresponding values of the inductance in the mast circuit and the inductance in the instrument circuit have a common difference of 2.60×10^{-5} henries as given by the intercept on the axis of ordinates. This difference is evidently the inductance between the point *M* and the earth by the path *MDIE*, Fig. 42. The experiment shows that for resonance the inductance of this path must have the fixed value 2.60×10^{-5} henries. By a separate experiment the value 2.62×10^{-5} henries was found for the inductance of this path when an open circuit was made at the point *B*. We have in this last case, however, the simple form of circuit examined in Experiment XII.

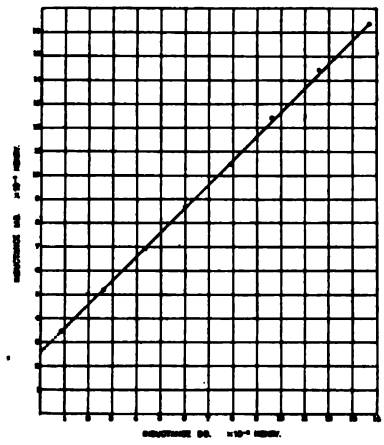

Fig. 44.

From these facts it appears, as should be seen by a glance at the circuit of Fig. 42, that the present experiment is dealing with the simple circuit of Fig. 31, with, however, an inductive[1] shunt inserted about the instrument. *The presence of the inductive shunt does not modify the resonance conditions. It simply diminishes the amount of energy obtained in the instrument.*

After the shunt has reached the value 6.0×10^{-5} henries its effect in this respect is small, so that the curves to the right of the curve with maximum ordinate 6.0, Fig. 43, have approximately constant amplitude, which is about 90 per cent. as great as the deflection obtained with the open circuit at *B*.

[1] The inductive shunt is subjected to inductive action from the current in the rest of the coil.

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XXII. EXPERIMENTS TO TEST THE IMAGE THEORY OF THE ACTION OF THE GROUND.

Grounded and Ungrounded Circuits. — The preceding experiments have all made use of grounded circuits at the sending and receiving stations. A number of wireless telegraph plants are in operation in which the circuits are not grounded. I am not aware that quantitative measurements have hitherto been made comparing the efficacy of the ungrounded circuits with the grounded.

In the experiments described below basis is afforded for at least a tentative comparison, although the experiments were undertaken primarily to illustrate the manner in which the ground acts, and the results are to be viewed chiefly as a test of the image theory of the grounded circuits.

Image Theory. — According to this theory a perfect ground introduces into the circuit a point of zero fluctuation of potential and, therefore, maximum fluctuation of current at the place where the ground is attached. The top of the antenna, on the other hand, is a point of zero current and maximum fluctuation of potential. In addition to these two end conditions the current and potential must obey certain differential equations throughout the length of the antenna. So far as concerns the part of the circuit above the earth, these conditions are the same as should obtain if the circuit instead of being grounded should be electrically mirrored in the earth. That is, the oscillation in the grounded circuit is simply the oscillation in one half of a symmetrical Hertz oscillator made up of the existing aerial system and its image, the image however contributing nothing to the radiation or reception of the waves.

To examine this view somewhat more in detail, let us confine our attention to the receiving station, and suppose we had there simply a rectilinear conductor isolated in space and placed parallel to the electric displacement of the incident waves. Let the length of the straight-line conductor be so chosen that its natural period of electric oscillation is equal to the period of the waves. The conductor would then be resonant with the incident waves. For a given strength of waves there would be a maximum current back and forth at the center of the conductor because on either side of the center there is the electrostatic capacity of half the conductor. At a point half way between the center and the end of the conductor

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the current back and forth would be less because out beyond this point the capacity is only the capacity of one fourth the conductor; while at the end of the conductor the current would be zero because there is no capacity beyond into which the current can flow.

We must now suppose that whatever current flows into one half of the conductor flows out of the other half; so that the potential at points in one half of the conductor rises while the potential of the other half falls. Thus the potential at the middle does not change, and the fluctuations of potential increase as we go toward either end. If we could introduce a current-reading detector into the circuit without disturbing the conditions, the instrument would give a maximum reading when placed at the center of the receiving conductor, that is, at the point where the fluctuation of potential is zero. Suppose with such an instrument in the circuit we should cut away one half the conductor; the reading would become zero. If now a capacity is attached to the instrument in place of the removed conductor, some current would flow between the straight wire and the capacity and register in the instrument.

If the capacity attached were very large (*e. g.*, the earth), the point of zero fluctuation of potential would again be brought near the instrument and we should have the same current as when the conductor was made up of two parts symmetrical about the instrument. Since, however, with the earthed circuit the antenna exposed to the radiation is only one half the original rectilinear conductor, to make the conditions identical we should have considered the other half of the original symmetrical system to be shielded from the action of the waves.

It is by reasoning of this kind, though usually expressed in mathematical form, that the theory is developed that the action in the grounded circuit with the receiving instrument near the ground is the same as it would be if instead of being grounded it should be symmetrically duplicated below the surface of the earth.

Of course, in actual systems the grounding is not perfect, and therefore, the symmetrical image gives only approximately an equivalent system.

This theory is submitted to tests in the experiments that follow, by comparing resonance curves with various forms of grounded

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circuits with the corresponding curves taken with an *image circuit* in the place of the ground.

Experiment XV. The Aerial Circuit and its Image Tuned by Variable Inductance. — In this experiment the sending station was the same as that employed in the preceding experiments (Fig. 30) and was constantly grounded. The arrangement of apparatus at the receiving station is shown in Fig. 45. By means of a switch at S the ground could be thrown off and replaced by metallic parts duplicating the aerial system. The duplicate is, however, not an exact image of the aerial system, because the second antenna had to be run horizontally instead of straight down.

The horizontal wire was made equal in length to the vertical antenna, 23.2 meters, and was supported about 1 meter from the

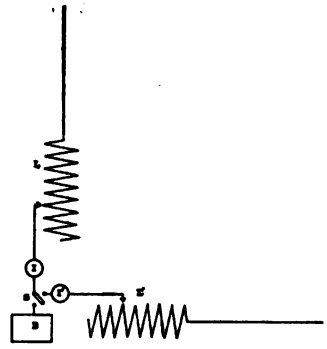

Fig. 45.

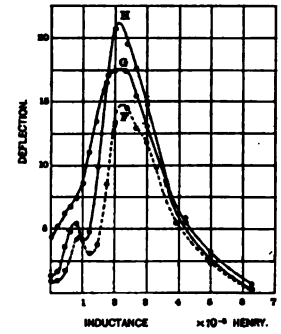

Fig. 46.

ground by cords attached to posts. In series with the horizontal wire was a variable inductance L' duplicating the tuning coil L and a small coil I' of fine wire, wound to duplicate the coil of the receiving instrument.

Curves giving the results of the experiment are shown in Fig. 46. For Curve G the grounded circuit was used, and readings of deflections were taken for various values of the inductance of the tuning coil L, Fig. 46; the deflections are plotted against values of L.

For curve H the switch was thrown so as to connect the aerial system with the horizontal system, Fig. 45, instead of with the ground, and deflections were taken for various values of L and its duplicate L' kept identical in value and varied together. In curve H the deflections are ordinates and the common values of inductance L and inductance L' are abscissas.

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Discussion of Results. — The two curves G and H, Fig. 46, are seen to have their maxima for the same abscissa. That is, a given value of inductance, 2.1×10^{-5} henries, gives a maximum deflection in the grounded circuit. To obtain a maximum with the duplicated system the same inductance 2.1×10^{-5} henries must be used in both the vertical circuit and its horizontal duplicate. This result is a confirmation of the image theory.

It is interesting to note that the *deflection* (*current square*) *is about 20 per cent. larger with the duplicated system than with the grounded system* — a fact that may be accounted for by supposing a higher resistance in the grounded system than in the wholly metallic system.

The resonance curve H taken with the wholly metallic circuit is somewhat different in shape from the curve G with the grounded circuit. The two curves agree well in shape for points to the right of the maximum, but for points to the left the curve with the grounded system slopes away more gradually and does not show the secondary maximum that is so marked with the duplicated system. That there is, however, a tendency to a secondary maximum in the former curve appears in a slight bulge in the curve and also in the fact that secondary maxima are shown by other members of the same family given in Fig. 32. The greater prominence of the secondary maximum of the curve H goes with the general greater sharpness of the curve as the result of the diminution of resistance accompanying the substitution of the metallic "image" for the ground.

After a number of preliminary tests in which the horizontal circuit was not made so close a duplicate of the aerial parts, the result shown in Fig. 46 seemed a rather striking agreement with the image theory.

In the effort to find a more convenient artificial ground than that supplied by the metallic duplicate of the aerial system the curve F was obtained, with the duplicate antenna wound around the house of the receiving station instead of extending out horizontal. In this case the capacity balancing the antenna was in the form of a rectangular spiral three meters square with a pitch of forty centimeters. This was a convenient arrangement, but was accompanied by a loss of some 20 per cent. of the energy received with the grounded circuit. Other arrangements, for example, a large number of short wires in the form of a horizontal fan, supported about one meter above the earth, gave about the same energy as that obtained with

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the metallic duplicate of the aerial circuit, that is 20 per cent. larger than the connection to earth.

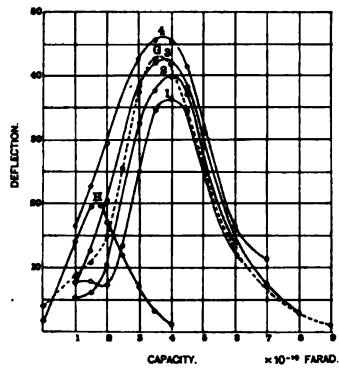

Fig. 47.

Experiment XVI. Tuning With Capacity in Shunt. — In further test of the image theory of the action of the ground, experiments were made with the capacity-shunt form of aerial circuit shown in Fig. 34. By throwing a switch this circuit could be grounded or completed by a metallic portion more or less nearly an image of the aerial system.

Curves are given in Fig. 47. The dotted curve *G* was obtained with the use of the ground; deflections are plotted against capacity about the instrument.

In taking the curve *H*, the ground was thrown off and a horizontal system was substituted for the ground. The horizontal system consisted of a duplicate of the coil of the instrument and a horizontal antenna 23.2 meters long. To have an exact duplicate there should be a variable condenser about the receiving instrument and an equivalent variable capacity about the duplicate of the instrument. As two such capacities were not easily available, instead of this arrangement the one variable condenser was put about both the instrument and its image. The curve *H* was obtained, in which deflection is again plotted against capacity of the shunt condenser. The maximum of *H* falls at a capacity one half the capacity for a maximum with the grounded circuit, *G*. This result confirms the image theory; for the condenser about the instrument and the image of this condenser in the duplicate system would be in series and therefore have together a capacity one half as great as the capacity for resonance with the grounded circuit.

In this experiment the deflections with the ungrounded circuit are a little less than half as great as the deflections with the grounded circuit. It is conjectured that this is due to the fact that our ungrounded circuit was not exactly a duplication of the original grounded system as may be seen from an examination of a diagram (not given) of the two arrangements. In the duplicated system a

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path is lacking for the current to go through the image capacity and then through the instrument.

Experiment XVII. Aerial System with Capacity Shunt; Image with Series Inductance. — In this experiment an aerial system with capacity shunted about the instrument (Fig. 34) could be grounded or could be connected to a horizontal system with variable inductance in series (Fig. 45). The curve *G*, Fig. 47, is a resonance curve with the grounded system. The curves 1, 2, 3 and 4 were taken with the ground replaced by the horizontal member, consisting of horizontal wire 23.2 meters long with various values of inductance in series with it, as follows:

Curve No.	Inductance in Horizontal Henries.
1	20×10^{-6}
2	27×10^{-6}
3	33×10^{-6}
4	39×10^{-6}

From the curves it is seen that the artificial ground that comes nearest to replacing the actual ground is the arrangement that gives curve 3. The horizontal portion of the circuit in this case is the same as the horizontal circuit and also the aerial circuit in experiment XV., for the common inductance in that case was 2.1×10^{-5} henries, which together with the duplicate of the instrument made a total inductance of 3.27×10^{-5} in each part of the circuit, which is in good agreement with the total inductance in the horizontal for curve 3, viz. 3.3×10^{-5} henries.

It should be remembered, however, that the curve 4 with greater inductance in the horizontal gives a larger deflection than that of curve 3 because with the greater inductance the point of maximum current is shifted into the instrument instead of being at the ground.

Experiment XVIII. Quarter Wave Ground. Determination of Wave-length. — The most interesting of the experiments confirmatory of the image theory of the action of the ground was made by replacing the ground by a straight horizontal wire of which the length could be varied. Resonance was obtained when this wire had the length of one fourth the wave-length.

Both the capacity-shunt and the inductance-series forms of aerial circuit were employed. These circuits were grounded and the capacity or inductance set for resonance. The ground was now

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disconnected and a long horizontal wire was attached in its place This threw the system out of resonance as shown by a small deflection. Wire was cut off the horizontal in steps and readings were taken. These readings increased as the horizontal was shortened up to a certain length and then decreased with further shortening of the horizontal. The results are plotted in Fig. 48. The curve *A* is with the inductance-series aerial; the curve *B* with the capacity-shunt aerial. The deflections were taken alternative with deflections with the circuit grounded and the ratio of the deflections with artificial ground to deflections with actual ground are plotted as ordinates against the length of horizontal as abscissas.

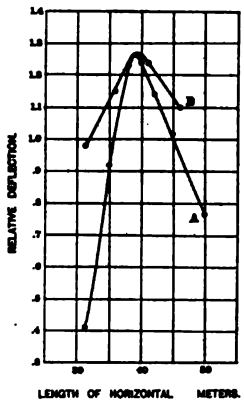

Fig. 48.

It is seen that in the experiments with both forms of aerial circuit the horizontal wire must have a length between 38 and 39 meters for a maximum deflection. If this is the quarter wave-length as the theory proposes, we should have for the wave-length a value between 152 and 156 meters, which is in excellent agreement with the value 153 meters found independently and by a different method in Experiment XIII.

Experiments XV., XVI., XVII. and XVIII. taken together show good agreement between the observations and the predictions from the image theory of the action of the ground. They also show that it is a simple matter to balance the aerial at the receiving station with an artificial ground that will increase the reception of energy (current square) by twenty per cent. or twenty-five per cent. over a good actual ground.[1]

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY, CAMBRIDGE, MASS.
October 17, 1905.

[1] The ground at each station consisted of three copper plates and a piece of iron pipe. The copper plates 60 cm. square by .3 cm. thick, were embedded in the earth 270 cm. below the surface. The pipe, 3 cm. in diameter and 180 cm. long was driven in until flush with the bottom of the holes containing the plates, and therefore reached to a depth of 450 cm. below the surface.

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THE EFFECT OF PRESSURE ON SURFACE TENSION.

By C. J. Lynde.

THE following article is an account of an investigation into the effect of pressure on the surface tension of the surface between two liquids.

Method. — Briefly, the method was to place the heavier of the two liquids in a U-tube, one arm of which was 1 cm. in diameter and the other a capillary tube; this was immersed in the lighter liquid, a pressure of from 1,000 to 6,000 lbs. per sq. in. was applied, and the change in the height of the meniscus in the capillary tube was observed by means of a micrometer microscope.

Apparatus. — The apparatus consisted essentially of: (1) A U-tube with one arm a capillary tube (Figs. 1 and 2). (2) A compression chamber, with plunger, screw, and gauge (Figs. 3 and 4). (3) Two windows opposite each other in the compression chamber, through which the movement of the meniscus could be observed.

The U-tubes (Figs. 1 and 2) were 14 cm. long, the larger upper tube being 9 cm. long and 1 cm. in internal diameter; the smaller tube connecting with the capillary tube was 5 cm. long and 0.5 cm. in internal diameter. The bore of the capillary tube varied for the different observations. Their diameters are given with the following tables.

The compression chamber *C* (Figs. 3 and 4) was of nickel steel 7.5 cm. square and 37 cm. long, the bore being 1.9 cm. in diameter. It was divided into two parts at *a* (Fig. 4) for the admission of the U-tube.

In the lower half, *w. w.* represent two cylindrical glass windows, 14 mm. deep and 14 mm. in diameter, cemented into hollow nickel steel plugs. The plugs were 33 mm. long, and 50 mm. in diameter at the head, and had a conical-shaped opening through the middle, which was 22 mm. in diameter at the head and 5 mm. in diameter at the windows. The upper half of the chamber screwed into

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the lower half, and a soft copper washer *A*, 2 mm. thick, served to make the juncture tight.

B is a large plug 48 mm. in diameter at the head and 50 mm. deep, which screws into the chamber. It has a hole through the center, through which the plunger passes.

P is a glass-hardened steel plunger 143 mm. long and 11.5 mm. in diameter.

D is a thin brass collar turned so as to fit the plunger accurately and so arranged (see Fig. 4) that the greater the pressure the tighter it holds.

S is the screw which gives the downward motion to the plunger; it is 105 mm. long and 15 mm. in diameter.

G (Fig. 3) is a gauge reading as high as 20,000 lbs. per sq. inch.

M is a micrometer microscope with focal length of 6 cm. and 11 divisions on the micrometer scale = 1 mm.; 100 divisions on micrometer head = 1 division of micrometer scale.

METHOD IN DETAIL.

Mercury and Water. — The U-tube (Fig. 1) was cleaned carefully before each set of observations, by boiling it in strong sulphuric acid and dropping fragments of potassium bichromate into the liquid, so that the gas liberated passed up through the capillary tube; then it was boiled in distilled water, then rinsed with cold distilled water.

The mercury was triple-distilled and had been passed through dilute nitric acid solution.

The distilled water was freshly boiled and cooled. The mercury was poured into the U-tube, then placed under water and some of it forced out through the capillary tube, so that air, if present, was removed and a fresh water mercury surface secured.

The U-tube was then placed in the compression-chamber and adjusted so that the meniscus was in the field of view of the windows *w*, *w*.

The chamber was closed, filled with water, and the plunger and compression-screw adjusted.

The method of observation in all cases was to set the movable cross-hairs of the micrometer microscope on the meniscus, and read

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its position. An assistant put on the pressure; the new position was read, the pressure was let off, and the position to which the meniscus returned was read.

Each individual reading in the tables is a mean of a movement with pressure and a return-movement when the pressure was released.

In the early experiments with mercury and water it was impossible to observe any movement of the meniscus, and even when the

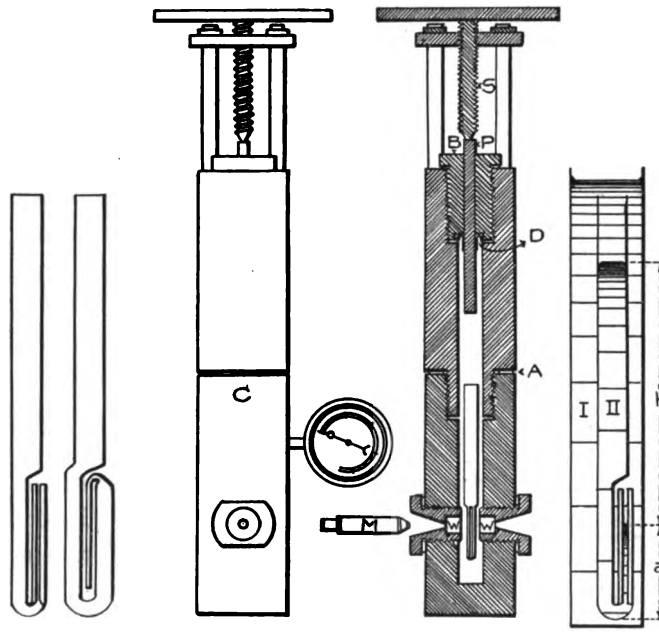

Fig. 1. Fig. 2. Fig. 3. Fig. 4. Fig. 5.

U-tube was taken in the hand and tilted from side to side the movement was slow and irregular. This was thought to be due to the formation of an oxide of mercury at the surface of contact. The difficulty was overcome by adding nitric acid to make the water a 3 per cent. acid solution.

The difference in level of the mercury columns h was measured by means of a cathetometer.

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METHOD OF CALCULATION.

Let T = surface tension of the contact surface.

θ = angle of contact.

h = difference in height in cm. of the columns of liquid II.

r = radius of capillary bore.

σ_1 = density of liquid I.

σ_2 = density of liquid II.

a = depth of liquid II. below meniscus.

Then

$$T \cos \theta = \frac{hr}{2}(\sigma_2 - \sigma_1). \times g \qquad (1)$$

In this equation each term may vary with the pressure.

The change in r can be neglected because, according to experiments of Amagat,[1] the linear compression of glass is .00000075 per atmosphere. The highest pressure used in this investigation was in the neighborhood of 400 atmospheres and this would produce a change in r of only .03 per cent., while the observed changes were all over 1 per cent. for this pressure.

From the experimental evidence at hand it appears that the contact angles of the surfaces employed in the present investigation are either 180° or in the neighborhood of 180°, so that a variation of θ with pressure will cause but a small variation in $\cos \theta$, and in the present discussion this variation has been neglected. To determine rigorously what effect pressure produces on $\cos \theta$ will require a further investigation.

The variables then are T, h, σ_1 and σ_2. The changes in σ_1 and σ_2 may be calculated from the coefficients of compressibility and the pressure. The change in h is that upon which the observations are made. From these the change in T is calculated in the following way:

Differentiating Equation 1 as to P

$$\frac{\delta T}{\delta P} \cos \theta = \frac{\delta h}{\delta P} \left\{ \frac{r}{2}(\sigma_2 - \sigma_1) + \frac{hr}{2}\left(\frac{\delta \sigma_2}{\delta P} - \frac{\delta \sigma_1}{\delta P}\right) \right\}$$

Dividing by Equation 1:

$$\frac{1}{T}\frac{\delta T}{\delta P} = \frac{1}{h} \cdot \frac{\delta h}{\delta P} + \frac{\overline{K}_2 - \overline{K}_1}{\sigma_2 - \sigma_1}.$$

[1] Wüllner, Vol. I., p. 238.

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In the present investigation δP represented a change of pressure of 1,000 pounds, $\therefore$ $\overline{K}_2$ and $\overline{K}_1$ represented the change in σ_2 and σ_1 for a change of 1,000 pounds in pressure.

Summary of Measurements.

1. r, the radius of the capillary tube, was measured by means of a micrometer microscope.

2. h, the difference of level of the liquid in the U-tube, was measured by means of a cathetometer. This difference of level could not be measured while the U-tube was inside the compression-chamber, because the field of view through the windows was not great enough to include the upper and lower surface at the same time. In consequence h was measured with the U-tube outside the compression-chamber.

3. a, the depth of the liquid in the U-tube below the meniscus (Fig. 5). This depth was also measured before the tube was placed in the compression-chamber.

4. $\delta h/\delta P$, the variation in height with change of pressure. The two surfaces could not be included in the field of view of the windows at one time. This was not necessary, however, for this measurement, because one arm of the U-tube being 10 mm. in diameter and the other arm of capillary dimension, a considerable change in the level of the surface in the capillary-tube would produce a very small change in the level of the surface in the larger tube. Thus the change in the height of the meniscus gave at once the value of $\delta h/\delta P$.

This method of measuring $\delta h/\delta P$, leads to the following correction.

Correction. — The liquid in the U-tube which was below the level of the meniscus contracted in volume when pressure was applied. As the contraction was the same in both arms of the U-tube, it would have introduced no error into the readings of $\delta h/\delta P$ if these readings had been made by observing the upper and lower surfaces at the same time. As, however, the reading of $\delta h/\delta P$ was made by measurements in the change of level of the meniscus only, an error was introduced. The correction was made as follows:

Let K = compressibility of the liquid per atmosphere at 25° C.
a = depth in mm. of the liquid below the meniscus (Fig. 5).

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p = pressure in atmospheres.

C = correction expressed in micrometer scale-divisions (11 divisions = 1 mm.).

C = 11 apk.

RESULTS FOR MERCURY AND WATER.

K for mercury per atm. at 25° C. = .000004; for water = .000041.

σ_2, density of mercury at 25° C. = 13.554; σ_1, water at 25° C. = .997.

a = 31 mm.

C = .09 divisions per 1,000 pounds.

$$100\,\frac{\bar{K}_2 - \bar{K}_1}{\sigma_2 - \sigma_1} = .022.$$

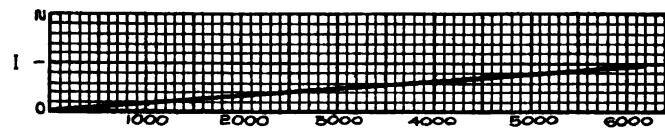
The readings are the observed changes in the height of the meniscus expressed in scale divisions. When the readings are such that they would indicate a decrease in the surface-tension, a — sign is used; otherwise, no sign is used.

Mercury and Water.

h = 44.1 mm.; diameters of the elliptical capillary bore 0.38 mm., 0.19 mm.

TABLE I.

Pressure in Lbs.	I.	II.	III.	IV.	V.	VI.	Mean.	Mean Corrected for Compression.	$\frac{100}{h}\cdot\frac{\delta h}{\delta P}$	$100\,\frac{\bar{K}_2-\bar{K}_1}{\sigma_2-\sigma_1}$	$\frac{100}{T}\cdot\frac{\delta T}{\delta P}$
1,000	1.69	1.75	1.07	.73	.63	.71	1.09	1.00	.20	—.02	.18
2,000	2.88	3.14	1.83	1.64	1.18	1.02	1.95	1.77	.36	—.04	.32
3,000	4.01	4.00	2.88	2.96	1.71	1.52	2.84	2.57	.52	—.06	.46
4,000	6.17	4.96	4.58	3.91	2.15	1.96	3.95	3.59	.74	—.09	.65
5,000	7.12	6.52	6.07	3.90	2.72	2.88	4.87	4.42	.90	—.11	.79
6,000	9.58	7.33	6.55	4.42	3.19	3.24	5.73	5.19	1.06	—.13	.93



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Mercury and Water.

Using a tube with a different capillary bore.

$h = 17.6$ mm.; diameter of capillary bore 0.59 mm.

$\frac{\delta h}{\delta P} = \frac{\text{number in "Corrected Mean" column}}{11}$

TABLE II.

Pressure in Lbs.	I.	II.	III.	IV.	V.	Mean.	Mean Corrected for Compression.	$\frac{100}{h} \cdot \frac{\delta h}{\delta P}$	$100 \frac{\bar{K}_2 - \bar{K}_1}{\sigma_2 - \sigma_1}$	$\frac{100}{T} \cdot \frac{\delta T}{\delta P}$
1,000 (Calc.)	.49	.30	.26	.52	.52	.42	.33	.17	−.02	.15
2,000	.72	.70	.59	1.04	1.13	.84	.66	.34	−.04	.30
3,000	1.52	.83	.83	1.69	1.69	1.31	1.04	.54	−.06	.48
4,000	1.96	1.02	.99	2.09	2.09	1.63	1.27	.66	−.09	.57
5,000	1.99		1.33	2.33	2.36	2.00	1.55	.80	−.11	.69
6,000	2.77	1.76	1.79	3.02	2.93	2.46	1.92	.99	−.13	.86

Eg: in 1st row:— $\frac{\delta h}{} = \frac{.33}{11}$

and $\frac{100}{h} \frac{\delta h}{\delta P} = \frac{100}{17.6} \times \frac{.33}{11} = .17$ ($\delta P =$ "1")

Conclusions.—(1) The surface-tension of the mercury-water surface *increases* with increase of pressure. (2) The percentage-increase is independent of the size of the capillary-tube. (3) The increase varies directly as the pressure.

Mercury and Ether.

Ether was substituted for water and the experiment repeated using the same tube as that for results in Table II. Here again it was necessary to add nitric acid to the ether, making it a three per cent. solution.

Corrections.—K for mercury $= .000004$, for ether $= .000185$; σ_2 for mercury $= 13.554$, σ_1 for ether $= .717$; $a = 31$ mm.; $C = .09$ scale-divisions per 1,000 lbs.;

$$100 \frac{\bar{K}_2 - \bar{K}_1}{\sigma_2 - \sigma_1} = -.095.$$

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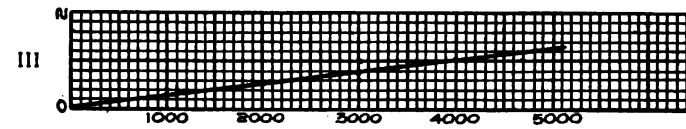
TABLE III.

$h = 12.75$ mm.; diameter of capillary tube $= .59$ mm.

Pressure in Lbs.	I.	II.	III.	IV.	Mean.	Mean Corrected for Compression.	$\frac{100}{h} \cdot \frac{\delta h}{\delta P}$	$100 \frac{\overline{K_2} - \overline{K_1}}{\sigma_2 - \sigma_1}$	$\frac{100}{T} \cdot \frac{\delta T}{\delta P}$
1,000	.63	.69	.74	.65	.68	.59	.42	−.09	.33
2,000	1.08	1.26	1.46	1.16	1.24	1.06	.76	−.19	.57
3,000	1.69	1.79	1.74	1.73	1.73	1.46	1.04	−.28	.76
4,000	1.95	2.79	2.46	2.05	2.31	1.95	1.40	−.38	1.02
5,000		3.32	2.91	2.32	2.85	2.40	1.71	−.47	1.23



Conclusions. — (1) The surface-tension of the mercury-ether surface *increases* with increase of pressure. (2) The increase varies directly as the pressure.

Water-Ether.

In this case it was found undesirable to let the ether come in contact with the compression-chamber, because it rapidly dissolved the De Khotinski cement used in the joints of the pressure-gauge and about the windows. A tube of the form given in Fig. 2 was therefore used.

Ether was placed in the tube and water surrounded it. An inverted ether-column, was thus formed in the capillary tube and adjacent side-tube.

The method of observation was as above.

Corrections. — K for water per atm. at 25° C. $= .000045$; for ether $= .000185$; σ_1 water per atm. at 25° C. $= .997$; σ_2 for ether $= .717$; $a = 8$ mm.; $C = 1.10$ divisions per 1,000 lbs.;

$$100 \frac{K_2 - K_1}{\sigma_2 - \sigma_1} = -3.40.$$

Results for Ether and Water: $h = 13$ mm.; diameter of capillary bore 0.59 mm.

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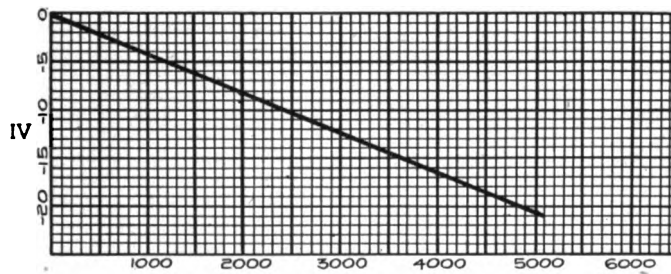
TABLE IV.

Pressure in Lbs.	I.	II.	III.	IV.	Mean.	Mean Corrected for Compression.	$\frac{100}{k} \cdot \frac{\delta k}{\delta P}$	$100 \frac{K_2 - \bar{K}_1}{\sigma_2 - \sigma_1}$	$\frac{100}{T} \cdot \frac{\delta T}{\delta P}$
1,000	.15	.32	.16	.20	.21	− .89	− .67	− 3.40	− 4.07
2,000	.40	.35	.32	.36	.36	−1.84	−1.39	− 6.80	− 8.19
3,000	.42	.40	.41	.38	.40	−2.90	−2.19	−10.20	−12.39
4,000	.52	.41	.44	.45	.45	−3.95	−2.99	−13.60	−16.59
5,000	.66	.56	.50	.59	.58	−4.92	−3.73	−17.00	−20.73



Graphical representation of the results given in Tables I.–V.

Conclusions. — (1) The surface-tension of the water-ether surface *decreases* with increase of pressure. (2) The decrease is proportional to the pressure.

Chloroform and Water.

Tube of form Fig. 1 used.

Corrections. — K for chloroform per atm. at 25° C. = .000062; for water = .000045; σ_2 for chloroform per atm. at 25° C. = 1.488; σ_1 for water = .997; a = 38 mm.; C = − 1.76 divisions per 1,000 lbs.;

$$100 \frac{K_2 - \bar{K}_1}{\sigma_2 - \sigma_1} = .235.$$

Results for Chloroform and Water: h = 22.5 mm.; diameter of capillary bore = 1.04 mm.

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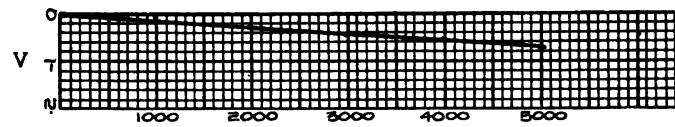
TABLE V.

Pressure in Lbs.	I.	II.	III.	IV.	Mean.	Mean Corrected for Compression.	$\frac{100}{h} \cdot \frac{\delta h}{\delta P}$	$100 \frac{\bar{K}_2 - \bar{K}_1}{\sigma_2 - \sigma_1}$	$\frac{100}{T} \cdot \frac{\delta T}{\delta P}$
1,000	.77	1.10	1.07	1.42	1.09	− .67	− .27	.23	−.04
2,000	1.10	1.57	1.73	2.01	1.56	−1.96	− .71	.47	−.24
3,000	1.70	2.02	3.09	2.64	2.36	−2.92	−1.18	.70	−.48
4,000	2.93	2.67	4.14	3.68	3.35	−3.69	−1.49	.94	−.55
5,000	2.54	4.07	4.86	4.92	4.09	−4.71	−1.90	1.17	−.73



Conclusion. — (1) The surface-tension of the chloroform-water surface *decreases* with the pressure. (2) The decrease is proportional to the pressure.

Carbon Bisulphide and Water.

The carbon bisulphide was Karlbaum's best redistilled three times. The tube used was of form Fig. 1.

Corrections. — K for CS_2 per atm. at 25° C. = .000087, for water = .000045; σ_2 for CS_2 per atm. at 25° C. = 1.265, σ_1 for water = .997; a = 20 mm.; C = − 1.30 divisions per 1,000 lbs.;

$$100 \frac{\bar{K}_2 - \bar{K}_1}{\sigma_2 - \sigma_1} = 1.36.$$

Results for Carbon Bisulphide and Water: h = 38.5. Diameter of capillary bore = 1.38 mm.

TABLE VI.

Pressure in Lbs.	I.	II.	III.	Mean.	Mean Corrected for Compression.	$\frac{100}{h} \cdot \frac{\delta h}{\delta P}$	$100 \frac{\bar{K}_2 - \bar{K}_1}{\sigma_2 - \sigma_1}$	$\frac{100}{T} \cdot \frac{\delta T}{\delta P}$
1,000	−3.11	−4.21	−2.71	−3.34	− 4.64	−1.09	1.36	.27
2,000	−5.78	−4.81	−4.41	−5.00	− 7.60	−1.79	2.72	.93
3,000	−7.27	−6.55	−7.00	−6.94	−10.84	−2.56	4.08	1.52
4,000	−8.71	−7.50	−7.22	−7.81	−13.01	−3.07	5.44	2.37

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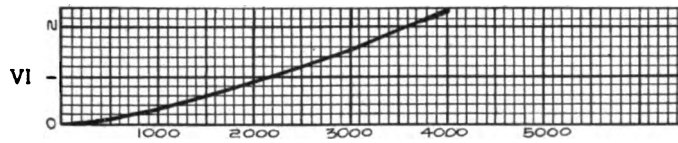

Conclusion. — The surface tension of the carbon-bisulphide-water surface *increases* with the pressure.

Conclusions.

1. The surface-tension of the contact-surface increases with increase of pressure in the cases of mercury-water, mercury-ether, and carbon-bisulphide-water.

2. The surface-tension of the contact-surface decreases with increase of pressure in the case of ether-water and chloroform-water.

3. The percentage-change is independent of the size of the capillary tube (Tables I. and II.).

4. The percentage-change is proportional to the pressure.

In conclusion I wish to thank Professor Michelson for suggesting the problem and the method of attack, and Professor Millikan for advice during the course of the work.

Ryerson Laboratory,
The University of Chicago.

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PROCEEDINGS

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THE ADJUSTMENT OF THE D'ARSONVAL GALVANOMETER FOR BALLISTIC WORK.[1]

BY FRANK WENNER.

DURING the past year I have used D'Arsonval galvanometers with a particular adjustment for ballistic work, and this adjustment has some very important advantages.

The coil is stripped of its dampers, so that its motion is but little damped when on open circuit. The relation between the coil constant, the suspension constant, the strength of the field, the moment of inertia of the coil and the resistance of the coil is so adjusted that the coil comes to the zero position in the least time without swinging past it. It is also desirable to have the period of the coil as large as 15 or 20 seconds. To make the period as large as this often requires the use of a small suspension or an increase in the moment of inertia of the coil. Unless the coil has a very large moment of inertia in proportion to the copper in it or swings in a very weak field the adjustment may be completed by putting the proper resistance in series with the coil. This resistance may be determined by using different values and observing the swing of the coil past the zero when released from a certain deflection. If resistances are plotted as ordinates and the swings past the zero as abscissa, the point where the curve meets the "y" axis gives the resistance.

With this adjustment the ballistic constant is e (base of Naperian log.) times as large with the coil on closed circuit as when on open circuit. The constant may be determined by the solenoid method, a condenser and standard cell or from its figure of merit and the free period of the coil. The galvanometer may be used either on closed or open circuit work with the same constant except the factor e. When used on condenser work the coil may be quickly brought to the zero by closing the coil circuit. When used on closed circuit work, such as iron testing and induction experiments, the coil returns to the zero position without attention about as fast as readings can be taken and recorded.

Other advantages which D'Arsonval galvanometers show for general work are also noticeable here.

[1] Abstract of a paper presented at the New York meeting of the Physical Society, Dec. 29–30, 1905.

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Volume XXII. *April, 1906.* *Number 4.*

THE

PHYSICAL REVIEW.

THE PHENOMENA OF IONIZATION IN FLAME GASES AND VAPORS.[1]

By F. L. Tufts.

Introduction.

In a previous paper on the phenomena of ionization in flames[2] the writer described a new method for studying the phenomena of electrical conduction through flame gases and vapors. The old method, employed by Sv. Arrhenius,[3] H. A. Wilson[4] and most other investigators of the electrical conductivity of flames, was to introduce into the flame under investigation clean platinum electrodes which became heated to incandescence by the flame. The conductivities of the flame gases and vapors between the electrodes were then compared by comparing the currents which a given impressed electromotive force would send through the flame.

All investigators found that under the above conditions the current increased less rapidly than the impressed electromotive force, and according to some, seemed to approach a saturation value. It was also found that for a given impressed electromotive force the current depended very largely upon the temperature of the electrodes, particularly that of the cathode, and was practically inde-

[1] A preliminary account of some of the work described in the present paper was given in the Physical Review, Vol. XX., p. 186.

[2] Phys. Zeitschr., Band 5, Heft 3, pp. 76–81.

[3] Wied. Ann., XLII., 1891.

[4] Phil. Trans. A., Vol. CXCII., 1899.

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pendent of the distance apart of the electrodes. This led some investigators[1] to advance the hypothesis that the ionization to which the conductivity of the flame was due, took place almost entirely at the surface of the glowing electrodes, and that throughout the volume of the flame there was little or no ionization.[2]

It was pointed out by the writer in the paper above referred to, that the total resistance encountered in the flame (R) may be considered in three parts, the resistance in the neighborhood of the cathode (R_k), the resistance in the neighborhood of the anode (R_a), and the resistance of the remainder of the flame between the electrodes (R_f) giving the equation $R = R_k + R_a + R_f$, and that if R_k or R_a were large in comparison with R_f, a variation in the distance apart of the electrodes would not change appreciably the value of R. Furthermore, it was shown that since R_k and R_a are functions of the conditions at the electrodes and of the current flowing between them, the above mentioned relations between current, electromotive force, and temperature of the electrodes, could be explained without denying the existence of a very considerable volume ionization throughout the flame.

The device employed by the writer for studying the electrical conductivity of flame gases and vapors has for its objects:

I. The reduction of the electrode resistances R_k and R_a to an order of magnitude equal to or smaller than that of the flame resistance R_f.

II. The maintenance of uniform conditions around the electrodes while the conditions throughout the conducting flame are being varied, as for example, by the introduction of the vapors of various salts.

III. The entire elimination of the electrode resistances, by determining the resistance, or conductivity, of a given section of the connecting flame from measurements of the current through that section and of the potential difference between the two faces of the section.

[1] H. A. Wilson, *ibid.*; J. J. Thomson, Conduction of Electricity through Gases, London, 1903, pp. 172 and 199.

[2] This view has been abandoned by H. A. Wilson in a recent paper, Phil. Mag., Vol. 10, No. 58, pp. 476–485, in which he takes the view of a volume ionization throughout the flame.

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The first of these objects was accomplished by the employment of platinum electrodes (*P*, *P*, Fig. 1) coated with calcium oxide and heated in separate electrode flames. Such incandescent electrodes of calcium oxide have been shown by Whenelt[1] to possess the property of offering a very slight resistance to the passage of an electric current to or from a conducting gas. The resistance of the electrode flames was made very small by supplying the burners

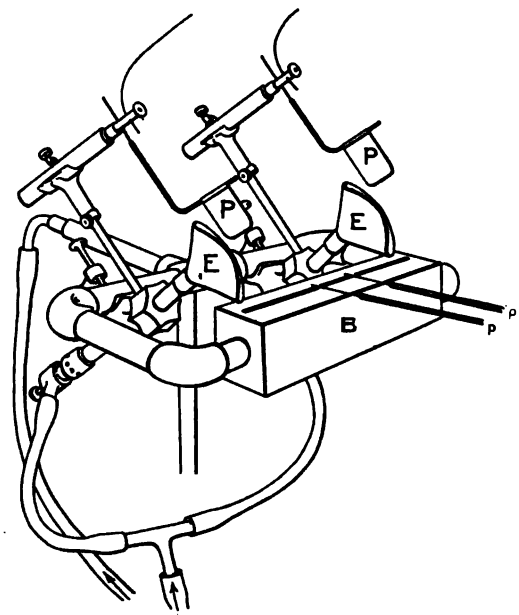

Fig. 1.

E, *E*, Fig. 1, with a mixture of gas and of air which had been blown through an atomizer containing a strong solution of potassium nitrate, the vapor of this salt being known to impart a very high degree of conductivity to the flame containing it. The flame under investigation was used as a connecting flame between the two electrode flames, and its resistance was made as great as possible by using, as a burner, a long narrow slot (0.1 cm. by 21 cm.) cut in a block of soapstone (*B*, Fig. 1). This burner gave a very broad, thin flame having a relatively large resistance.

[1] Ann. der Phys., Band 4, Heft 14, p. 425, 1904.

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The second object was accomplished by having the supply of gas and air for the connecting burner independent of the supply for the electrode burners, so that the conditions in the connecting flame could be altered without in any way changing the conditions around the electrodes. The gas and air supplied to the connecting flame were both passed through suitable meters so that the volume of either consumed per minute could readily be measured. The type of meter used consisted of a small circular opening in a thin, metal diaphragm so mounted that the difference of pressure on the two sides of the diaphragm, when a current of gas or air was flowing through the opening, could be accurately measured by an inclined *U*-tube manometer containing xylene. A schematic diagram of one of these meters is shown in *M*, Fig. 8. Each meter was calibrated by connecting it in series with a standard gas meter, and the values of the manometer readings were determined in cubic feet per minute when gas or air was blown through. The conditions in the connecting flame could thus not only be varied independently of the electrode flames, but the volumes of gas, air, or spray supplied to the burner could readily be measured.

To accomplish the third object, the current through the flame was measured by connecting in series with the electrodes (*PP*, Fig. 1), a galvanometer of the d'Arsonval type, sensitive to about 10^{-8} amperes and provided with a universal shunt. The electromotive force employed was furnished by a battery of dry cells, and could be varied between about 1.5 and 200 volts. The difference of potential between the two faces of any section of the connecting flame was determined by inserting two fine, platinum wires (*pp*, Fig. 1) near the tip of the inner blue cone, and at a distance apart equal to the breadth of the section under investigation. The wires were connected respectively to the needle and to the middle point of the series of batteries used to impress a fixed difference of potential between the quadrants. Under these conditions the deflections of the electrometer needle were directly proportional to the difference of potential between the wires *pp* for all values of the potential to be measured.

The difference of potential between the wires *pp* was shown by the following experiments to be a true measure of the difference of

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potential between the corresponding points in the flame. The introduction into, or withdrawal from the flame, of the electrometer wires, was found to produce no change in the current through the flame of as much as one per cent. of its value. The difference of potential across a breadth of 6 cm. of the connecting flame was measured by means of the electrometer wires in three steps of 2 cm. each, and again in a single step of 6 cm. the two measurements were found to agree within the errors of the readings. A further test of the correctness of the potential difference obtained by the use of the electrometer wires was made by measuring with them the potential difference across the connecting flame and also the difference of potential between either electrode plate and one of the electrometer wires inserted at the boundary between the electrode flame and the connecting flame. The sum of the three differences was found to be equal to the electromotive force impressed at the electrodes.

Measurements of the potential difference between the cathode plate and the flame around it under various conditions showed that this difference increased much more rapidly than the current between the electrodes, and it was found that by using a long connecting flame, a small impressed electromotive force (one or two volts) and a saturated solution of KNO_3 in the atomizer supplying the electrode flames the resistances at the electrodes could be made so small in comparison with the resistance of the connecting flame that they could be neglected without introducing any appreciable error. Under these conditions the conductivity of the connecting flame could be taken as directly proportional to the current for a given impressed electromotive force. In some cases it was found more convenient to determine relative conductivities in this way than by the use of the electrometer wires. A comparison of the two methods, however, showed that in all cases they gave the same results.

In this paper the term "conductivity of a given section of the connecting flame" will be used to designate the quotient obtained by dividing the current through the flame by the potential difference between the two faces of the section. Since the connecting flame was not rectangular in shape, but was more or less irregular

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in its upper boundary, the lines of current flow and the equipotential lines in the connecting sheet of flame are not straight but are slightly curved, and therefore the "given section" above referred to is not a rectangular section. As, however, the measurements, were all relative, the shape of the section was unimportant so long as it remained the same. Furthermore, it was found that the size and shape of the upper portions of the flame had little or no influence on the total conductivity, as over 90 per cent. of the current was carried by the lower portions of the flame quite near the slot of the burner.

The experiments described in this paper have been made with flames consuming ordinary illuminating gas. The measurements are mostly relative, and the paper is more in the nature of a qualitative investigation into the source of ionization in flame gases and vapors than a quantitative study of the same. The writer hopes soon to be able to make a more quantitative study of the phenomena. The measurements already made have, however, led to a number of very important general relations which are given in the following sections.

I. A Saturation Current not Possible in the Combustion Cones of the Ordinary Bunsen Flame.

Some experiments were undertaken by the author in connection with Dr. J. Stark[1] for the purpose of ascertaining whether a saturation current could be obtained between two platinum wire electrodes, either clean or coated, with CaO placed very close together in the Bunsen flame. The results showed conclusively that no trace of a saturation current could be obtained under these conditions, but that for impressed electromotive forces of over 100 volts, the current increased more rapidly than the electromotive force. Under these conditions it was not possible to determine the relation between current and potential gradient in the flame, since the gradient could not be considered as uniform between the electrodes.

Later some experiments were undertaken by the author, in which the long connecting flame was used between the two electrode

[1] Phys. Zeitschr., Band 5, Heft 9, pp. 248–257.

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flames. Various electromotive forces, up to 8,000 volts, were impressed at the electrodes, and the potential gradient and corresponding current in the connecting flame were measured as described in the introduction, the electrometer wires being placed in the inner blue cone of the flame and about 4 cm. apart. For

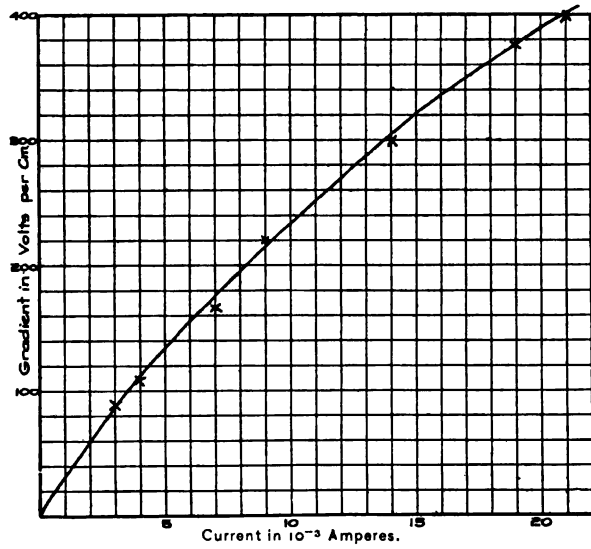

Fig. 2.

potential gradients ranging between 0.1 and 50 volts per cm., the current was found to increase directly as the potential gradient, the relation being a simple linear one. For gradients between 100 and 400 volts per cm., the current was found to increase more rapidly than the potential gradient. The results are shown in the curve, Fig. 2. When the impressed electromotive force was still farther increased, there were unmistakable evidences of ionization by impact, such as a sudden increase in the current, a decrease in the potential gradient and a marked increase in the temperature of the electrodes and of pieces of mica or platinum that might be placed in the connecting flame.

Experiments were also tried in which the electrode flames and the electrometer wires were placed in the outer blue cone of the connecting flame instead of in contact with the inner blue cone. The results, however, were similar to the above, showing that within

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the combustion cones of the flame it is not possible to obtain a saturation current. Within these regions the rate of production of ions is so great that ionization by impact is produced before the potential gradient is great enough to remove the ions as fast as formed.

II. Electrical Conductivity of the Different Cones of the Bunsen Flame.

For the purpose of studying the electrical conductivity of the different parts of the Bunsen flame, a separable cone burner was constructed by placing over the slot in a soapstone burner similar to *B*, Fig. 1, a rectangular chimney of soapstone 1 cm. wide on the inside and 9 cm. high. Through small holes in the ends of the chimney, copper wires were inserted carrying thin platinum foil electrodes coated with CaO. The electrometer wires were inserted through small holes in one side of the chimney, about 4 cm. apart and directly between the electrodes. The holes were so spaced that the electrodes and the electrometer wires could be placed in either of the following positions: (1) In the inner blue cone, (2) in the space about a centimeter above the inner blue cone, (3) in the space just below the outer blue cone, (4) above the chimney in the outer blue cone.

In each of the above positions the electrometer wires were placed 4 cm. apart and directly between the electrodes, which were ordinarily kept about 8 cm. apart. The currents and the corresponding potential differences between the electrometer wires were measured in each of the above positions for a number of different impressed electromotive forces. The following are representative of the results obtained:

Position 1. — With a potential gradient of 12 volts per cm., the current was 2.7×10^{-4} amperes, and increasing the gradient increased the current in the same proportion.

Position 2. — A potential gradient of 9 volts per cm. gave a current of 4.5×10^{-7} amperes, and doubling the potential gradient increased the current to only 6.0×10^{-7} amperes.

Position 3. — A potential gradient of 10 volts per cm. gave a current of 3.5×10^{-8} amperes, and doubling the potential gradient did not appreciably increase the current.

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Position 4. — A potential gradient of 9 volts per cm. gave a current of 2.1×10^{-6} amperes, and increasing the potential gradient increased the current proportionately.

On comparing the specific conductivities of the different parts of the flame from the above data, it should be kept in mind that the cross-sections of the blue cones carrying the currents in positions 1 and 4 were much smaller than the cross-sections of the intermediate gases carrying the currents in positions 2 and 3. The difference in specific conductivity between the blue cones and the intermediate gases is, therefore, even greater than would appear from the above data. From these data it appears that the specific conductivity of the gases in the inner blue cone of the Bunsen flame is about 1,000 times greater than the specific conductivity of the gases in the region just above the blue cone, and about 10,000 times greater than the specific conductivity of the same gases after ascending some 7 or 8 cm. above the lower cone. The measurements also show the specific conductivity of the inner cone to be about 100 times that of the outer cone.

While the measurements in the combustion cones showed no indication of a saturation current, the measurements made in the region between the two cones showed unmistakably the possibility of such in this region.

These measurements would seem to show that in the Bunsen flame, the source of the ionization is the chemical process of combustion taking place in the two cones of the flame, and that between and outside of these cones we have recombinations of the ions produced in the cones. Therefore the number of free ions per c.c. in the ascending gas diminishes rapidly as the gas is carried away from the regions of combustion.

In the case of the ordinary luminous gas flame where no air is mixed with the gas before it reaches the burner, it was found that the conductivity of the upper luminous portion of the flame was very small in comparison with the conductivity of the colorless, or faintly blue, lower portion. This was shown by introducing a sheet of mica across the flame so as to cut in two the upper luminous portion, when it was found that the current was not appreciably diminished. If, however, the mica were lowered so as to cut into

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the lower non-luminous portion, the current was decreased and became zero when the mica sheet touched the burner. This shows that the chemical reactions taking place in the lower non-luminous portions of the ordinary gas flame are the ones chiefly productive of ionization, and that the consumption of the carbon particles in the upper luminous portions of the flame is accompanied by a relatively small amount of ionization.

III. Relation Between the Character of Combustion in a Gas Flame and its Electrical Conductivity.

The next experiments were for the purpose of comparing the electrical conductivities of flames consuming the same quantity of illuminating gas per minute, but having mixed with the gas various quantities of air or carbon-dioxide, so as to change the character and appearance of the flame. The burner used was the long, slot burner *B*, Fig. 1. Measurements of the conductivity of the ordinary, luminous type of gas flame and of the Bunsen type of flame consuming the same volume of gas per minute showed that the Bunsen flame possessed from one and a half to two times the conductivity of the luminous flame. When the volume of gas supplied to the burner was kept constant, and gradually increasing amounts of air mixed with it before feeding it to the burner, the character of the flame changed gradually from the luminous to the Bunsen type. In this transition five rather distinct types of flame could be recognized by the eye. The diagrams in Fig. 3 show roughly the

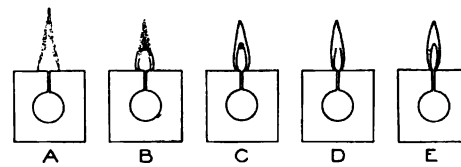

Fig. 3.

appearance of cross-sections of the different types. The ordinany, luminous type of flame is shown in *A*, no air being mixed with the gas before it was fed to the burner. The addition of air caused the flame to become shorter and change gradually to the type represented in *B*, which showed some rudiments of an inner blue cone,

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and that portion of the carbon luminosity immediately above the inner cone seemed to be more luminous and of a less reddish hue than the rest. When the volume of air added was about equal to the volume of gas, the carbon luminosity had disappeared, with the exception of a faintly luminous cap to the rather feeble inner blue cone, type *C*. The further addition of air destroyed this luminous cap, and when the volume of air was something over twice the volume of gas, a cross-section of the flame had much the appearance shown in *D*. The inner blue cone seemed to have no well developed cap. The further addition of air caused the flame to assume the Bunsen type, *E*, and on continuing to increase the supply of air, the only effect was to cause the combustion cones to contract around the mouth of the burner.

Measurements were made of the conductivity of a given section of the above flame as gradually increasing amounts of air were added to a constant supply of gas of 0.18 cu. ft. per minute. The relation between conductivity and rate of supply of air is given

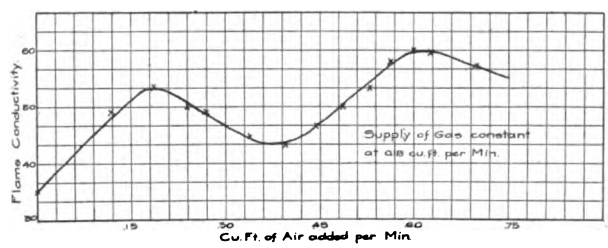

Fig. 4. Supply of Gas Constant at 0.18 cu. ft. per minute.

in the curve, Fig. 4. The measurements showed that the change in the character of the flame from type *A* to type *C* was accompanied by an increase in its conductivity, while the change from type *C* to *D* caused a decrease in conductivity. After the full development of the inner blue cone, the further addition of air caused the conductivity to increase to a maximum and then to decrease again, but rather slowly, as the velocity of efflux of the gases from the burner becomes greater and the combustion cones smaller.

A close relation between the character of the combustion taking place in a flame and its electrical conductivity was to be expected after the experiments described in section II., which showed that the

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process of ionization was practically confined to the combustion regions of the flame, and was dependent on the type of combustion taking place in those regions. The number of free ions per cubic centimeter in any combustion region depends, however, in all probability, not only on the character of the chemical reactions taking place in that region, but also on the temperature and possibly the dilution of the gas in the region of combustion. Some such assumption would seem to be demanded for the explanation of the following phenomena:

When gradually increasing amounts of CO_2 instead of air were mixed with a fixed volume of the illuminating gas before delivery to the burner, the effect was to decrease the carbon luminosity and give a flame consisting of a single, thin, blue combustion sheet on either side of the burner slot. Measurements on the conductivity of the flame showed, however, no marked variation in conductivity until enough CO_2 had been added to destroy all the carbon luminosity, when the further addition of CO_2 caused a gradual decrease in the conductivity. The decrease was approximately proportional to the increase in the rate of supply of CO_2.

IV. Relation of Flame Conductivity to Rate of Consumption of Gas.

Measurements were next made for the purpose of determining the relation between the conductivity of a given section of the connecting flame and the rate of consumption of gas by the flame. For flames of ordinary illuminating gas unmixed with air (type *A*, Fig. 2), and consuming over a few hundredths of a cu. ft. of gas per minute, the relation between conductivity and rate of consumption of gas was found to be a linear one, although, for rates of consumption of over 0.15 cu. ft. per minute, with the burner used, the flame became very smoky. A typical set of readings is given in Fig. 5.

The conductivity of a shorter section of the connecting flame was measured for rates of gas consumption ranging from 0.01 cu. ft. to 0.16 cu. ft. per minute. For rates of consumption less than a few hundredths of a cu. ft. per minute, with the burner used, the flame consisted of a single blue cone with no carbon luminosity.

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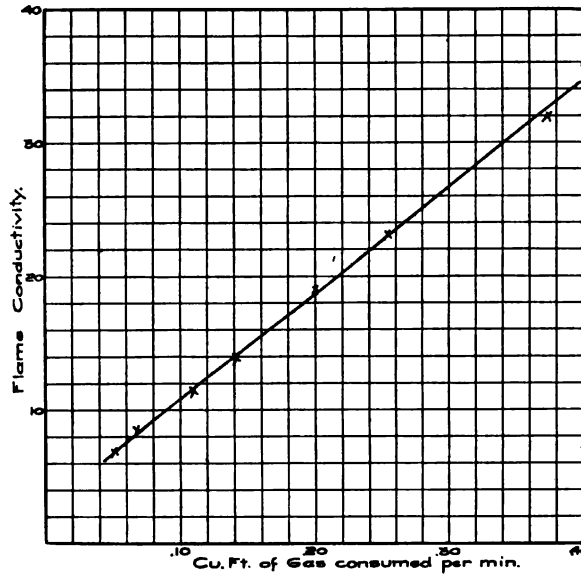

Fig. 5.

The character of the flame changed to the ordinary luminous type as the rate of supply of gas was increased. The relation between

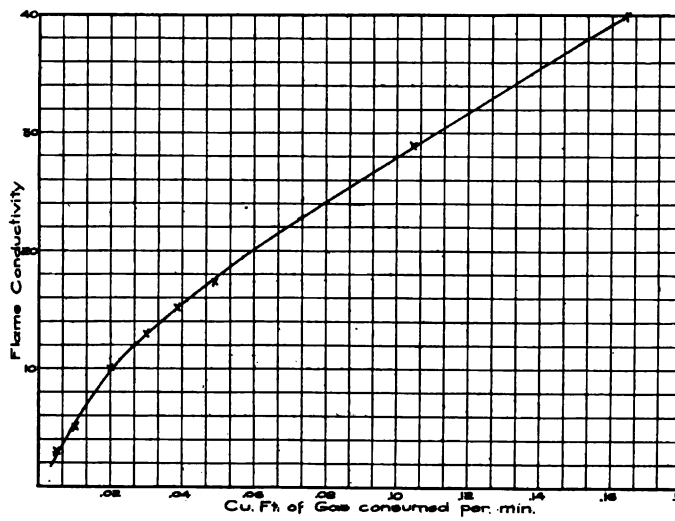

Fig. 6.

the rate of consumption of gas and the electrical conductivity of the flame is shown by the curve in Fig. 6. It was found that at first,

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for the non-luminous flame, the conductivity increased quite rapidly with the rate of supply of gas. As the carbon luminosity became more pronounced the conductivity increased less rapidly, and finally, after the development of a flame of type *A*, Fig. 2, the relation between conductivity and rate of gas consumption became practically a linear one.

Other experiments were made in which air was mixed with the illuminating gas before feeding it to the burner, and as the supply of gas was increased, the supply of air was increased in the same proportion, so as to keep the ratio of air to gas a constant. This gave the same type of flame for all rates of supply of gas. Under these conditions measurements were made of the conductivity of the connecting flame for various rates of consumption of gas and for different ratios of gas to air. The result of a typical set of readings is

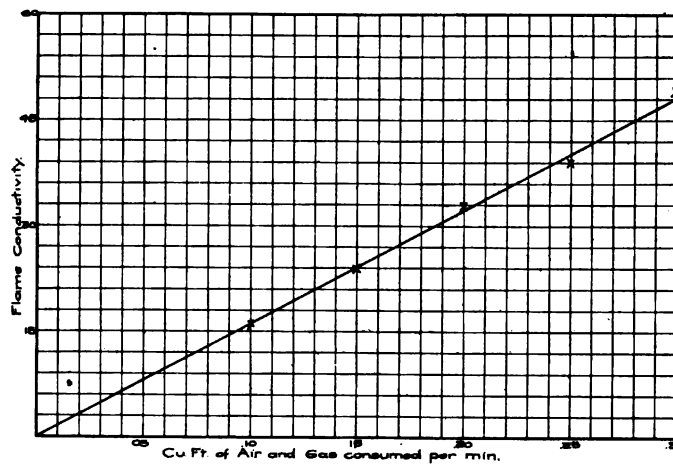

Fig. 7.

given in Fig. 7, the volume of air being equal to the volume of gas. So long as the character of the flame was kept the same and the ratio of gas to air remained constant, the electrical conductivity of the flame was found to increase directly with the rate of consumption of gas by the flame.

The above simple relation between the electrical conductivity and the rate of supply of gas to a flame is readily explained if we assume that for a given type of combustion the number of free ions per

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cubic centimeter within the region of combustion remains constant. Increasing the rate of supply of gas to the burner would cause a proportional increase in the cross section of the combustion zone, and the electrical conductivity would increase directly as the area of this cross section.

V. Conductivity Imparted to a Flame by Salt Vapor.

Investigations on the conductivity imparted to a gas flame by the introduction of spray from a solution of salt were carried on by means of the apparatus shown in Fig. 8. The spray from the solu-

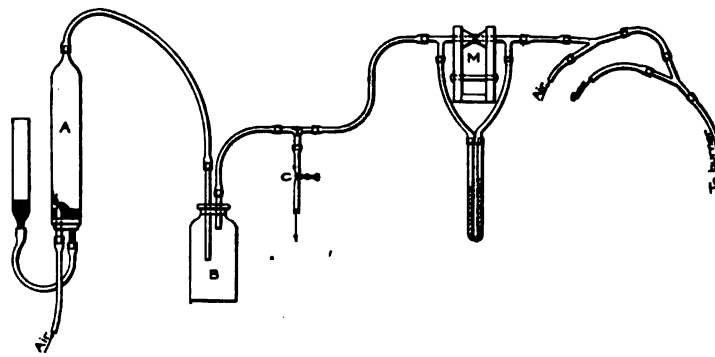

Fig. 8.

tion under investigation was obtained by passing a current of air or illuminating gas through an atomizer (*A*) containing the solution. The spray from the atomizer was led into a settling bottle (*B*) where the larger drops carried over from the atomizer were deposited. The spray was then conveyed through a T-tube to a meter (*M*) and thence to a Y-tube where it could be mixed with definite volumes of air or gas before being delivered to the burner. The diaphragm in *M* could readily be changed, and by means of the pinch-cock *C*, the flow of spray could be so regulated that for any size of opening in the diaphragm the difference in pressure on the two sides could be kept constant without changing the pressure on the atomizer. Under these conditions it was found that the flow through the diaphragm was directly proportional to the area of the opening. This device afforded two means of varying in a measurable manner the quantity of salt introduced into the flame: (1) Keep-

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ing the opening in the diaphragm and the difference in pressure between the two sides the same, the concentration of the solution in the atomizer could be varied; (2) keeping the same solution in the atomizer, the size of the opening in the diaphragm in *M* could be altered and varying quantities of the spray admitted to the flame.

The conductivity imparted to the flame by the salt spray was determined by subtracting from the total conductivity determined in the usual way, the conductivity of the flame when consuming an equal amount of gas and of air which had been blown through the atomizer when it contained water in place of the salt solution. Whether the air was saturated with water vapor or dry seemed to make no difference in the conductivity of the flame.

Preliminary measurements showed that the conductivity imparted to the connecting flame by the introduction of salt spray varied greatly according to the character of the flame. Measurements of the relative conductivities imparted to a flame by different quantities of salt spray were also found to be quite different for the different types of flame. It therefore seemed desirable to investigate more carefully the effect that variations in the character of the flame would have on the salt conductivity imparted to the flame by a given amount of spray.

Experiments were undertaken for the purpose of determining the effect on the salt conductivity of gradually increasing the supply of gas to the burner while keeping the rate of supply of air and of salt spray constant. Increasing the supply of gas caused the flame to change gradually from a forced Bunsen flame of type *E* to a flame of type *B*, very rich in carbon luminosity. The rate of supply of air and spray from the atomizer through the meter (*M*, Fig. 8) was kept constant at 0.23 cu. ft. per minute. Measurements were made of the salt conductivity imparted to the flame by the spray from a solution of NaCl as increasing quantities of gas were mixed with the spray. The measurements were repeated when solutions of different concentrations were placed in the atomizer, the rate of supply of air and spray being kept constant at 0.23 cu. ft. per minute. The results are shown in the curves in Fig. 9. An examination of the curves shows that the salt conductivity increases at first very rapidly with the increase of gas. It reaches a maximum

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when the rate of supply of gas is about equal to the rate of supply of air through the atomizer, giving a flame of type *C*. The salt conductivity then decreases, but very slowly, as the rate of supply

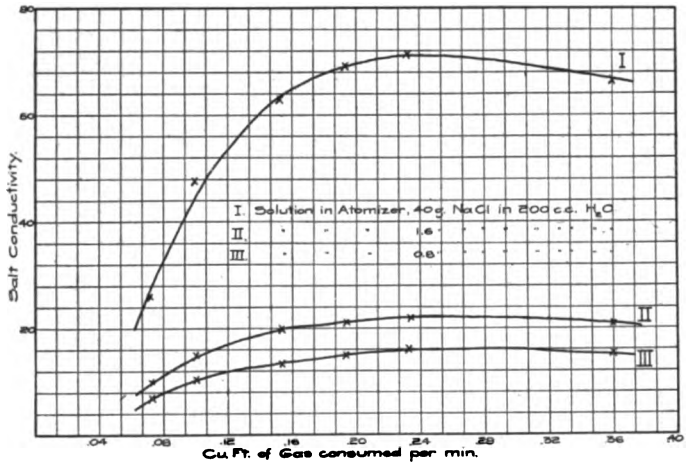

Fig. 9.

of gas is increased. A change in the concentration of the salt solution in the atomizer does not change the general character of the above relation.

Other experiments were tried in which the salt spray was introduced into the flame by blowing the gas itself through the atomizer. The supply of gas and spray from the atomizer was kept constant and gradually increasing amounts of gas supplied to the burner by a separate tube. Under these conditions the salt conductivity imparted to the flame remained almost constant, although the cross-section of the flame, due to the addition of the gas, was increased several times.

Other measurements of the salt conductivity imparted to the flame were made when the rate of supply of spray was kept constant and the rate of supply of gas and of air both increased in such a way as to keep the total volume of air equal to the volume of gas supplied. Under these conditions it was found that the salt conductivity increased directly with the rate of suppy of air and gas for all solutions of moderate concentration. When a very concentrated solution of NaCl was placed in the atomizer, the salt conductivity

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imparted to the flame seemed to increase somewhat less rapidly than the rate of supply of air and gas. The results of measurements made with three different concentrations of salt solution in the

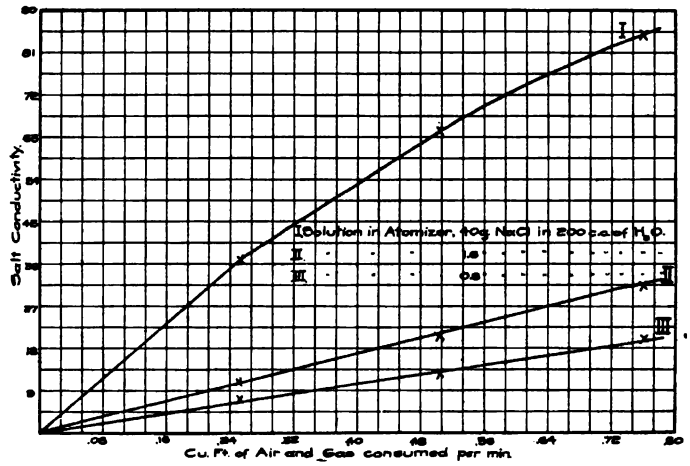

Fig. 10.

atomizer are given in the curves of Fig. 10, the volume of air was kept equal to the volume of gas supplied.

In the next experiments the illuminating gas itself was blown through the atomizer, and the rate of supply of gas and spray to the burner was kept constant at 0.17 cu. ft. per minute. The conductivity of the flame was then measured, as gradually increasing amounts of air were mixed with the gas and spray before delivery to the burner. Under these conditions the character of the flame changed from a flame of type *A* through the intermediate types to a forced Bunsen flame of type *E*. The measurements of the gas conductivity when pure water was placed in the atomizer are given

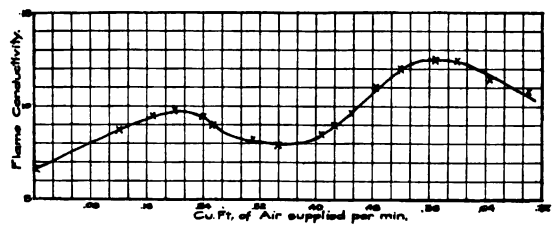

Fig. 11.

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in the curve in Fig. 11. The measurements of the salt conductivity imparted to the same flame when solutions of NaCl of different concentrations were placed in the atomizer are given in the curves of Fig. 12. An examination of the figures shows that the mixture of

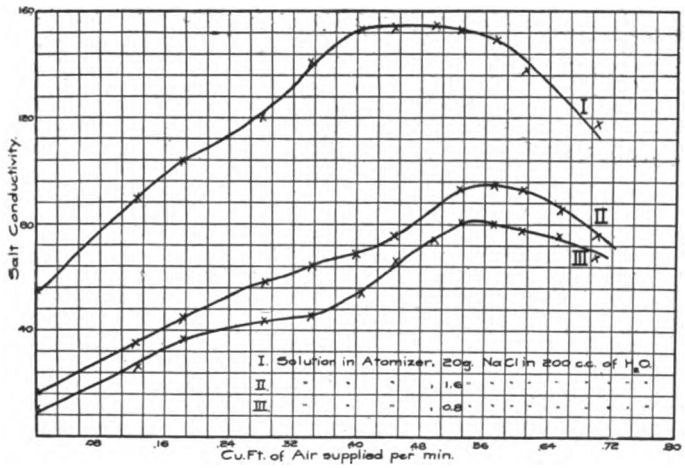

Fig. 12.

air and gas which gives the maximum conductivity to the pure flame gives also the maximum of salt conductivity. The addition of air to a flame of type *A* containing salt spray causes the salt conductivity to increase at first with the quantity of air added. This increase continues until the rate of supply of air is about equal to the rate of supply of gas, when the farther addition of air causes a less rapid increase in the salt conductivity until enough air has been added to give a flame of type *E*. Continuing the addition of air causes a more rapid increase in the salt conductivity which finally reaches a maximum when the volume of air is between three and four times the volume of gas. The ratio between this maximum of salt conductivity and the conductivity imparted by the same quantity of salt to the flame of type *A* when no air was mixed with the gas, was found to be quite different when different concentrations of the salt solution were used in the atomizer. The following are the ratios obtained :

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Number of Grams of NaCl Dissolved in 200 cc. of H_2O.	Ratio of Maximum Salt Conductivity Imparted to a Flame of Type *E* to the Conductivity Imparted to a Flame of Type *A* Consuming the Same Quantity of Gas.
20	2.9
1.6	5.7
.8	6.8

These numbers show that the variation in the salt conductivity due to a variation in the character of the flame, on the addition of air, is much greater when the quantity of salt in the flame is small than when it is large. The increased quantity of salt ions in the flame seems to diminish in some way the effects of the changes tending to bring about an increase in ionization.

Experiments were also made in which gradually increasing amounts of pure oxygen instead of air were added to a fixed rate of supply of gas and spray. The results were of a similar character to those obtained by the use of air.

Another set of measurements was made in which gradually increasing amounts of CO_2 in place of air were added to the fixed rate of supply of gas and spray from the atomizer. For very dilute solutions of NaCl in the atomizer, the addition of CO_2 caused no change in the salt conductivity imparted to the flame until enough CO_2 had been added to destroy the carbon luminosity, when the farther addition of CO_2 caused a decrease in the conductivity. For the more concentrated solutions in the atomizer the salt conductivity seemed to decrease with the first addition of CO_2. The results of measurements made with three different concentrations of salt solution are given in the curves of Fig. 13. The rate of supply of gas and spray was kept constant at about 0.17 cu. ft. per minute.

Experiments were made with the separable cone burner described in Section II., when a large quantity of spray from a saturated solution of NaCl was mixed with the air and gas before delivery to the burner. Measurements of the current and potential gradient were made in the positions 1, 2, and 4 (see Section II.), with the following results:

Position 1.—With a potential gradient of 7 volts per cm. the current was 7.5×10^{-4} amperes.

Position 2.—A potential gradient of 0.7 volt per cm. gave a current of 7.5×10^{-6} amperes.

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Position 4. — A potential gradient of 10 volts per cm. gave a current of 75×10^{-6} amperes.

In all these positions an increase in the potential gradient was accompanied by a proportional increase in the current. If, from the

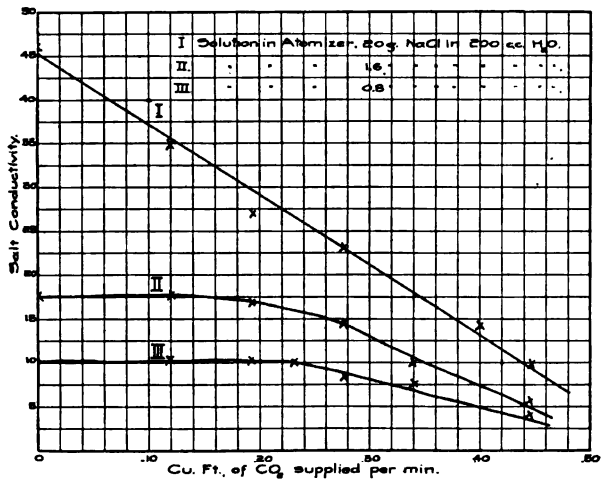

Fig. 13.

total conductivity of the different cones given above, we subtract the conductivity due to the flame gases given in Section II., we shall have numbers expressing, approximately, the salt conductivity imparted to the different cones of the flame. In this way it was found that the conductivity imparted to the inner blue cone by the salt spray was about ten times the conductivity imparted by the spray to the region just above the inner cone, and about two hundred times the conductivity imparted to the outer blue cone. The difference between the salt conductivity of the inner blue cone and the conductivity in the region between the two cones is seen to be very much less than for the flame gases themselves. (See results given in Section II.)

It seems difficult, if not impossible, to account for the phenomena described in this section on the assumption that the ionization of the salt spray in the flame is due simply to the high temperature of the flame. The temperature at a given point in the region of combustion in a flame of type *A* can certainly not decrease with the increase in the supply of gas to the flame. There would there-

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fore be no good reason for assuming that the rate of production of salt ions per cu. cm. in this region of combustion would be diminished by increasing the supply of gas if the ionization were due simply to the temperature. Increasing the supply of gas would however, increase the cross-section of the combustion zone, so that one would naturally expect an increase in the total salt conductivity imparted to a flame of type *A* on the addition of gas. The experiments showed that the salt conductivity remained practically a constant for widely varying rates of supply of gas. When, however, a flame of type *C* was obtained by mixing air with the gas, the salt conductivity did increase in almost direct proportion to the amounts of gas and air added (see Fig. 10). Furthermore, the addition of air to a flame of type *A*, the rate of supply of spray and gas being kept constant, was shown to cause an increase in the salt conductivity (see first parts of curves in Fig. 12).

The above seems to warrant the conclusion that in order to have the salt spray ionized in the flame one must have not only the high temperature of the flame, but also the mixture of the spray with oxygen. Other conditions remaining the same, the salt conductivity imparted to a flame by the introduction of salt spray can be increased by the addition of air or oxygen.[1]

VI. Relation Between Salt Conductivity and the Rate of Supply of Salt to the Flame.

Experiments were next undertaken for the purpose of determining the effect on the salt conductivity of increasing the rate of supply of spray to a flame of type *B* consuming gas at a fixed rate. Three methods were tried for varying the rate of supply of spray.

1. The diaphragm in the meter *M*, Fig. 8, was changed and the pinch-cock *C* so adjusted that for different openings in the diaphragm the difference in pressure on the two sides remained constant. Under these conditions the rate of supply of spray to the burner could be increased by increasing the rate of supply of air in the same proportion. The constant rate of supply of gas to the burner was large enough to give a flame of type *B* for even the largest amount of air and spray. Under these conditions it was

[1] Some further results are given in the PHYSICAL REVIEW, Vol. XXII., page 113. On page 114, the 16th line from the top, instead of $Na = 6$, it should read $Na = 3$.

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found that with rather concentrated solutions of NaCl in the atomizer, the salt conductivity imparted to the flame increased directly with the volume of spray supplied to the flame. With very dilute solutions, however, the salt conductivity seemed to increase a little more rapidly than the rate of supply of air and spray. The

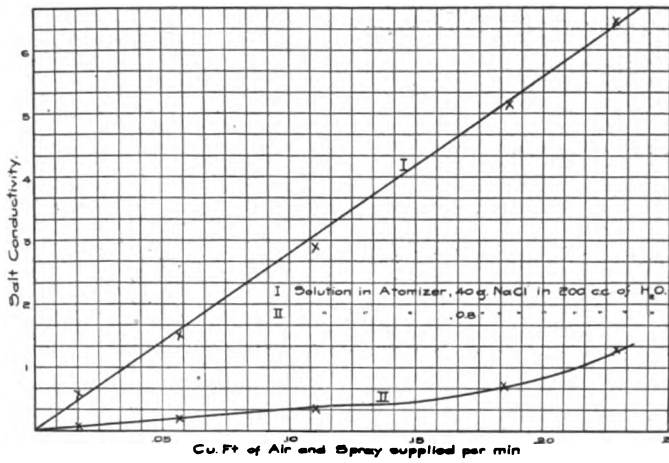

Fig. 14.

results of measurements made with two solutions of very different concentrations are given in the curves of Fig. 14.

2. In the above method of varying the supply of spray to the flame, the proportion of air to gas was also varied. To avoid this, a second method of varying the rate of supply of spray was tried in which, by means of an independent supply of air, the quantity of spray delivered to the flame could be varied without changing the proportion of air to gas.

3. A second method of accomplishing the same result would be to vary the concentration of the salt solution in the atomizer, keeping other conditions the same. Both of these methods were tried, and the results are given in the following table. The flame in both cases was of the type *B* having the volume of air less than the volume of gas.

The numbers in the first vertical column of the table are proportional to the salt conductivities imparted to the flame by the spray from a very concentrated solution of NaCl (40 g. in 200 c.c.),

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when the area of the opening in the diaphragm was respectively 1, $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$ and $\frac{1}{24}$ of the area of the largest opening used. The numbers in the other vertical columns are proportional to the salt conductivities when solutions of $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$ and $\frac{1}{24}$ of the concentration of the above were used in the atomizer. The numbers in the horizontal rows of the table, therefore, are proportional to the salt conductivities imparted to the flame by spray from the different solutions when the area of the opening in the diaphragm remained the same.

Concentration of Salt Solution.

Area of Diaphragm Opening.	1	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{24}$	Ratio of Maximum to Minimum Salt Conductivity Due to a Variation in the Concentration of the Solution.
1	94	77	60	43	25	3.8
$\frac{1}{2}$	73	55	41	28	16	4.6
$\frac{1}{4}$	53	41	29	20	11	4.8
$\frac{1}{8}$	34	26	18	12	6	5.7
$\frac{1}{24}$	16	12	9	6	2.5	6.4
Ratio of Maximum to Minimum Salt Conductivity Due to a Variation in the Diaphragm Opening.	5.9	6.4	6.7	7.2	10.0	

The numbers representing the conductivities imparted to the flame by small quantities of the salt vapor are liable to a larger percentage of error than the numbers representing the larger conductivities. They were obtained, like the other numbers, by subtracting from the total flame conductivity the conductivity of the flame when water was placed in the atomizer instead of the salt solution. For small quantities of salt in the flame, however, the total conductivity was of the same order of magnitude as the conductivity of the flame with water in the atomizer, and since it was found difficult to maintain absolutely uniform conditions in the flame, these

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small differences are liable to a possible error of as much as 25 per cent. for the very smallest conductivities.

In the vertical column to the right of the table are given the ratios between the salt conductivities imparted to the flame by a given volume of spray from the concentrated and from the most dilute solution. In the row of figures below the table are given the ratios between the salt conductivities imparted to the flame by the largest and the smallest volumes of spray from the solutions of different concentrations. An inspection of these ratios shows that as the total quantity of salt in the flame is decreased, the same percentage variation of the quantity causes a much larger percentage variation in the salt conductivity imparted to the flame. In other words, increasing the quantity of salt in the flame seems to retard the process of ionization.

A further inspection of the ratios shows that for certain rates of supply of the salt spray to the flame, the conductivity varies approximately as the square root of the rate of supply, but that for larger rates the variation is less rapid than the square root law would give, and for smaller rates it is more rapid. A number of measurements were made of the salt conductivity imparted to a flame of type *B* when a very dilute salt solution was used in the atomizer — about $\frac{1}{700}$ concentrated. They showed that under these conditions the conductivity was almost directly proportional to the rate of supply of the spray.

The experiments of this section give additional evidence in favor of the conclusion arrived at in the last section. The linear relation between salt conductivity and rate of supply of salt spray when the rate of supply of air was increased proportionately (see Fig. 14) shows that the presence of oxygen plays as important a rôle in the phenomena of ionization of the salt spray as the high temperature of the flame.

When the rate of supply of gas and air was kept constant and the rate of supply of salt spray was increased, the experiments showed that for extremely small rates of supply of the spray, the salt conductivity increased in almost direct proportion to the rate of supply of the spray. As the quantity of the salt in the flame became larger, however, the conductivity was found to increase much

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less rapidly than the rate of supply of salt. This would seem to be due to a decrease in the proportion of oxygen to salt spray, owing to which, a smaller proportion of the spray is ionized.

VII. Relation between Luminosity and Conductivity Imparted to a Flame by the Vapor of a Salt.

In a previous paper[1] the writer described some experiments on the relation between the luminosity and the conductivity imparted to a flame of the Bunsen type by the vapor of NaCl or of LiCl, when the luminosity was varied by the introduction of the vapor of chloroform, and it was shown that the relation was practically a direct one, the vapor of the chloroform reducing the conductivity in the same proportion as it reduced the luminosity.

The relation between luminosity and conductivity has also been determined when the luminosity was varied by varying the amount of spray introduced into the flame, either by changing the concentration of the solution in the atomizer or by changing the size of the opening in the diaphragm in *M*, Fig. 8. The sodium luminosity of a section of a low thin flame of the Bunsen type was determined by forming an image of the section on the slit of one of the spectroscopes of a Brace spectrophotometer, the filament of an incandescent lamp being used before the other slit for comparison. The conductivity of the same section of the flame was determined in the usual way by inserting the electrometer wires about 1 cm. apart and one on either side of the section. A number of simultaneous measurements of the conductivity and luminosity imparted to the flame by the vapors of either sodium or lithium chloride showed that varying the quantity of vapor in the flame by changing either the concentration of the solution in the atomizer or the size of the opening in the diaphragm in *M*, Fig. 8, or both, caused the luminosity to vary in the same proportion as the conductivity. In all these measurements the salt conductivity and luminosity were determined by subtracting from the total, the conductivity or luminosity due to the flame when water was placed in the atomizer. The measurements shown in Fig. 15, for NaCl, are representative of the results obtained.

[1] Phys. Zeitschr., Band 5, Heft 6, pp. 157–159.

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A number of other measurements were made when a sheet of mica, which was found to be quite free from sodium, was inserted

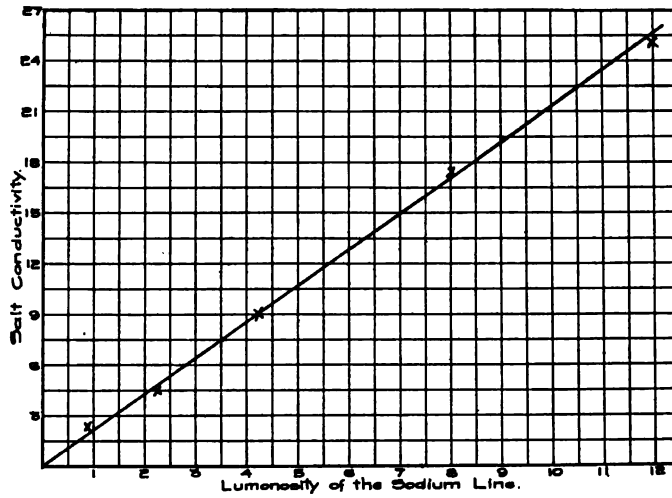
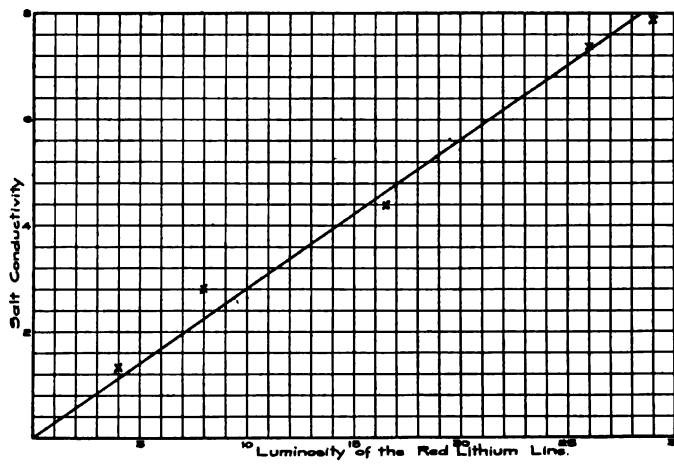


Fig. 15.

across the flame so that the lower edge of the mica was about 1 cm. above the burner. The electrometer wires were placed about half



F g. 16.

a centimeter apart, one on either side of the mica, and just above the burner. An image of the section of the flame between the lower

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edge of the mica and the burner was formed on the slit of the spectroscope. Simultaneous measurements of the luminosity and conductivity imparted by the salt vapor to this section were made when the character of the flame was varied by varying the supply of air and gas, and keeping the rate of supply of spray to the flame constant. The relation between luminosity and conductivity, under these conditions, was also found to be a simple, linear one. A representative set of measurements for LiCl is given in Fig. 16. The conductivity measurements for the lithium salts are liable to a larger percentage error than those for sodium, owing to the smaller conductivity imparted by lithium salts to the flame.

The foregoing results show that when the luminosity imparted to a gas flame by the vapor of either sodium or lithium chloride is varied by varying the rate of supply of salt or by varying the character of the flame, the electrical conductivity imparted to the flame by the salt vapor is varied in the same proportion.

The relation between the electrical conductivity and the luminosity imparted to a flame by the spray from a solution of $CaCl_2$ did not seem to be so simple a one as for the salts of lithium and sodium. Owing to the relatively small conductivity imparted to the flame by the salts of calcium the measurements are liable to a larger percentage error and no very satisfactory results have as yet been obtained.

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CONDUCTIVITY OF VAPOR FROM THE MERCURY ARC.

By C. D. Child.

THE ease with which an electric current passes through the vapor of a mercury arc is well known. The experiments here described show that the vapor in the neighborhood of the arc also has a high conductivity and that the cause of the ionization there found is perhaps different from the causes of ionization which have heretofore been studied. The experiments were commenced for the purpose of finding the velocity of the ions in the mercury arc by the method which had been used in studying their velocity when drawn from a flame,[1] but it was found that in the case examined new ions are produced in all regions in the neighborhood of the arc, so that the method is not applicable. The investigation was, therefore, turned to a study of these ions.

Apparatus. — The apparatus used is shown in Fig. 1. *A* and *B* are two bulbs containing the mercury, the arc being formed by the common method of tipping the tube. *C* is a platinum wire used to draw the ions from the arc, *D* is one to determine the potential near to *C*, and *E*, to determine the potential of the arc.

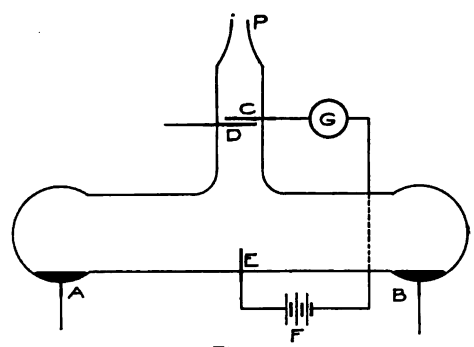

Fig. 1.

The potential difference between *C* and *E* was produced by the battery *F* and the current between these points was measured by the galvanometer *G*. *P* is the connection to the pump.

[1] Phys. Rev., 12, 65.

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There is an objection to this arrangement in that E does not have the same potential as the arc about it, except when no current is flowing from E. A different arrangement was tried by putting a shunt between A and B and placing the battery and galvanometer between C and the middle of this shunt. But it was found that the middle of the arc did not have the same potential as the middle of the shunt. This was shown by placing an electrometer between the two points. Moreover the potential of E was continually varying. Whenever the mercury in A or B moved or even when the end of the arc shifted over the mercury, the potential of E changed. As a result the arrangement shown in the figure was used. This at least, gave results somewhat consistent with themselves and its disadvantages did not interfere with showing the principal facts for which this form of the apparatus was used.

The length of the tube was 13 cm. and the inside diameter 2.1 cm. The platinum wires were .45 mm. in diameter. The branch tube was 1.4 cm. in diameter. The distance of C from the middle of the tube AB was 6 cm.

Current between C and E Dependent upon Time.—On examining the current between C and E, it was found that when the arc was first started, the current was small; that it rapidly increased, and then decreased. This increase varied much at different times, but as an example a set of readings taken when the potential difference between C and E was 13 volts is given in Table I. The current through the arc was 4.5 amperes, and the pressure of the gas .2 mm. The first column gives the length of time that the arc had been running; column 2, the current when C was positive; and column 3, when it was negative.

TABLE I.

Time in Sec.	Current when C was Positive.	Current when C was Negative.
5	28×10^{-4}	5.7×10^{-4}
10	55	2.8
20	130	1.7
30	110	1.2
60	51	.57

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The change in the current was not caused by the charge on C, for the conductivity was found to vary the same whether C was charged positively or negatively or was uncharged. It was found that the current became large much sooner, if the tube was hot when the arc was started, also that a glow gradually crept up the tube from the arc, and the conductivity became much greater when the glow reached C. The front of this appeared to be the boundary region between the hot mercury vapor and the residual gases which it was pushing out, for in this region the drops of mercury first began to appear on the sides of the glass.

Effect of Changing the Potential Difference. — Next the potential difference between C and D was varied, keeping the other conditions the same as before. With each potential difference the largest current which was observed at any time is given. Column 1 gives the potential difference; column 2, the current when C was positive; column 3, that when it was negative.

TABLE II.

Potential Difference between C and E.	Current with C Positive.	Current with C Negative.
1.5		5.1×10^{-4}
2.5		5.1
5	20×10^{-4}	5.4
8	68	5.4
11	100	5.4
13	128	5.4

With the first two voltages given with C connected to the positive side of the battery the current flowed against the E.M.F. of the cells, showing that there was an E.M.F. between C and E greater than 2.5 volts. E.M.F.'s of more than 13 volts were not used, because with so large currents the potential difference between E and the arc must become appreciable.

When the battery was placed between C and the middle of a shunt about AB, the results were much the same, except that with potential differences about 12 or 13 volts and with C positive, an arc was liable to form having C for the positive end.

The Internal E.M.F. between C and E. — The internal E.M.F.

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between C and D was examined by balancing it against a variable potential difference. C was found to be negative at first, becoming positive, however, before the maximum conductivity of the gas occurred, and remaining positive.

A set of data taken are given in Table III. Column 1 gives the time in seconds from the starting of the arc and column 2, the E.M.F. in volts. The minus sign indicates that C was negative with respect to E. After the first four observations C was positive.

TABLE III.

Time in Sec.	E.M.F. in Volts.	Time in Sec.	E.M.F. in Volts.
9	−2	99	3.3
16	−3	106	3.5
33	−1.5	112	3.6
40	−1	121	3.8
44	+ .5	133	4
52	2.3	144	4.3
67	2.6	163	4.5
75	2.7	178	4.6
89	3	209	4.4

Several sets of observations were taken all similar to this. In general the change from negative to positive occurred sooner than in the data given above. It occurred at approximately the same time as that at which of maximum conductivity occurred.

The Potential Difference between C and D. — The potential difference between C and D when a current was flowing between C and E was examined by a quadrant electrometer. It was found that when the arc was first started the potential difference between C and D was nearly as great as that between C and E. After a few seconds it gradually decreased until the former was about half of the latter. This shows even more conclusively that the gas itself, aside from the layer about the electrode C, has a very high conductivity.

The experiments thus far bring out clearly three facts; first, that the gas in the branch tube is highly conducting; second, that this conductivity is greatest when the luminous part of the vapor first reaches the electrode; and third, that there is an E.M.F. in the branch tube.

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Ions do not Come from the Arc. — The next experiments were undertaken for the purpose of determining whether the current between *C* and *E* was carried by ions coming from the arc, or by ions produced in the neighborhood of *C*. The branch tube was replaced by one having four electrodes as shown in Fig. 2. *CD* and *EF* were connected to separate E.M.F.'s which could be varied at will. If the current was carried by ions coming from the arc, it was expected that they would all be drawn out of the vapor by *CD* leaving none for *EF*.

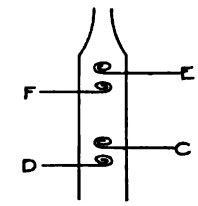

Fig. 2

In the experiment as tried the distance from *C* to the middle of the main tube was 5 cm.; from *D*, 5.5 cm.; from *E*, 8.3 cm.; and from *F*, 8.8 cm. The wires were platinum wires .45 mm. in diameter and coiled as in the diagram. The pressure of the gas remaining in the tube was .1 mm.

The current through *CD* was first examined and it was found that this current varied appreciably with the time and that it also depended on the direction of current between *C* and *D*. There is given in Table IV. the current at different times. Column 1 gives the number of seconds after the arc was started; column 2, the corresponding current in amperes, when *C* was positive; and column 3, that when it was negative. The E.M.F. in the circuit was 13 volts.

TABLE IV.

Time in Sec.	Current with *C* Positive.	Current with *C* Negative.	Time in Sec.	Current with *C* Positive.	Current with *C* Negative.
10	2.8×10^{-4}		85		17×10^{-4}
15		23×10^{-4}	90	5.1×10^{-4}	
20	14		95		10
25		45	100	2.8	
30	28		105		8.5
35		68	110	2.3	
40	40		115		5.7
45		85	120	1.7	
50	45		125		4.5
55		91	140	1.1	
60	34		145		3.4
65		63	160	1.1	
70	14		165		2.8
75		28	180	1.1	
80	8.5		185		2.3

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It was noticed in making these observations that the time of maximum conductivity occurred a few seconds after the luminous part of the tube reached *CD*. Again the maximum current between *E* and *F* occurred shortly after the luminosity first reached that part of the tube.

The current through *CD* was then tested to learn whether it was "saturated." The data are given in Table V. Column 1 gives the potential difference between *C* and *D* in volts; column 2, the maximum current in amperes which flowed at any time with *C* positive; and column 3, that with *C* negative.

TABLE V.

Potential Difference.	Current with *C* Positive.	Current with *C* Negative.
1.2	24×10^{-4}	32×10^{-4}
2.5	42	62
5	42	83
9.5	49	97
13	57	110

The current between *C* and *D* would then appear to be "saturated" with only 5 volts, the increase after this, no doubt, being due to the fact that with stronger fields ions which are produced at greater distances from the electrodes are drawn up to them.

The current between *E* and *F* was found to vary in the same way, although it was at all times less than that between *C* and *D*, and the difference between the current flowing from *E* to *F* and that from *F* to *E* was not nearly as great as the difference in the two directions between *C* and *D*. The maximum current between *E* and *F* was 14×10^{-4} ampere.

The current through *EF* was further examined first when a current was flowing through *CD* and then with this current removed. The potential difference between *C* and *D* was 13 volts. This was more than enough to "saturate" the current, so that we had reason to believe that all of the ions passing between *C* and *D* were removed when this potential difference was applied. The current between *E* and *F* was, however, found to be the same whether any was flowing between *C* and *D* or not.

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The current through *EF* was next tried together with a current through *CF*, *EF* being connected to an E.M.F. of 1 volt and *CF* to 13 volts, *F* being positive with respect to both *C* and *E*. In this case the current through *EF* was decreased from .95 to .85 milliampere, when the connection was made for the current to flow between *E* and *D*.

It would thus appear that none of the ions which carry the current between *E* and *F* come from the part *CD* and that but few of them are produced between *C* and *F*; that is, in general the ions found outside of the arc do not come from the arc, but are produced in the immediate neighborhood of the place where they are found.

Current not over Surface of Glass. — In all of these experiments there has been nothing to prove that the current did not flow over the surface of the glass. It is conceivable that the hot mercury vapor should make the surface a conductor. A coil of steel wire which pressed tightly against the surface of the glass, was, therefore, inserted between *C* and *D* as in Fig. 3. This was connected by a platinum wire to the outside at *E*. *C* was also extended so as to pass through the coil without touching it. *C* and *D* were then

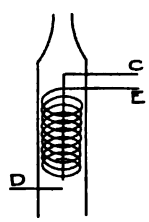

Fig. 3.

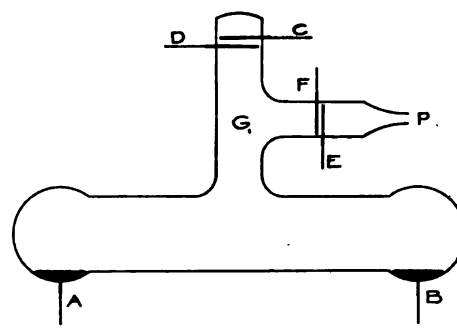

Fig. 4.

connected as before through a galvanometer and a cell, a storage cell of 2 volts was used in this case. It was found that the current between *C* and *D* was the same (approximately .002 ampere) whether *E* was kept at the potential of *C* or at that of *D*. This showed conclusively that the current passed through the gas and not over the surface of the glass.

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Current not Caused by Rays from Arc. — It was thought that possibly rays were being given off from the arc that were making the space above it conducting. An experiment was, therefore, tried with a tube as in Fig. 4. The distances between *C* and *D* and between *E* and *F* were both approximately .5 cm. The distance from *D* to *G* was 3.5 cm. and that from *F* to *G* 4 cm. *P* was connected to the pump. Both *CD* and *EF* were connected to a galvanometer and a gravity cell.

It was found that an appreciable current first began to flow through *CD*, but that after 15 or 20 seconds the current between *E* and *F* became the larger. These experiments indicate that the ions are not produced by rays from the arc, otherwise the current between *C* and *D* in Fig. 4 would be the larger.

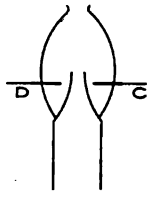

Fig. 5.

A tube was made as in Fig. 5, but with this there was no luminosity between *C* and *D*, nor was there any appreciable current between them at any time.

The experiments, therefore, show that the current does not flow over the surface of the glass, that it is not carried by ions from the arc, and is not produced by rays from the arc.

E.M.F. between C and D. — Examination was then made of the E.M.F. between *C* and *D*. It was measured by balancing it against a variable potential difference as when measuring E.M.F. between *C* and *E*. It was found that this E.M.F. behaved quite differently under different circumstances. When the electrodes were two coils of wire as in Fig. 2, the upper one was continually negative.

In one experiment it happened that the E.M.F. was observed when the upper electrode was a coil of platinum wire as before and the lower one a straight platinum wire as *C* in Fig. 1. With this arrangement the upper one was first positive and then negative, and finally positive again. This was found with three different tubes.

However in another tube with a similar coil above and a straight wire below and with other conditions the same, as far as was known, there was only one change of sign of the E.M.F., the coil being first positive and then negative. The data taken with this tube are given in Table 6, column 1 giving the time in seconds, and column 2, the E.M.F. in volts.

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TABLE VI.

Time in Sec.	E.M.F. in Volts.	Time in Sec.	E.M.F. in Volts.
30	+.30	108	−.17
38	+.07	119	−.28
55	+.07	125	−.38
68	+.04	155	−.43
80	−.04	185	−.40
89	−.07	220	−.35
98	−.11		

It is not known why these different results were obtained. The pressure of the gas left in the tube was approximately .1 mm. in each case. There were some reasons for believing that the amount of water vapor left in the tube had some effect, but this has not yet been proven. The effect is no doubt due in some way to the greater mobility of the negative ions, but it is difficult to see just how this could produce the observed results. It needs, in fact, a much more careful study than I can at present give it, in order to give any satisfactory explanation.

Cause of the Ionization. — We see that the experiments have shown that the conductivity of the gas is produced neither by the ions from the arc, nor by rays from the arc. At first it was thought that the ions were produced by the high temperature, mercury vapor possibly ionizing more easily than other gases. The temperature, however, is not very high, and we have as yet no proof that even very high temperatures will produce ionization.

A different explanation has been suggested by Prof. Ernest Merritt, one which has much in its favor. According to this, when ions first recombine, their union is more or less incomplete. Each ion before recombining may have been a cluster of atoms with a positive or negative charge added. Two such oppositely charged clusters might become attached without the charges coming into the intimate relation which is needed for complete equilibrium. Some of these incomplete combinations might again break up much as the atoms of radium are supposed to do when subjected to some unusual atomic force. We might look upon such a group of atoms as radio-active matter produced artificially. Such a group would not be acted on by electrical forces, so that they would pass *CD* in

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Fig. 3 and yet might be split up again into ions by the time they had reached *EF*.

It seems quite possible that such groups would be more apt to be formed with a mixture of gases at comparatively low temperature than with a single gas at high temperature. This would explain the fact that the conductivity of the gas is the greatest in the region where the mercury vapor is condensing. This is the boundary region consisting of the residual gases left in the tube and the mercury vapor which would be pushing them on. In the parts of the tube nearer the arc the continual flow of mercury vapor would have carried the other gases out and there would be nothing but mercury vapor and this would be at a high temperature. This is the region which we find has but small conductivity.

The E.M.F. Oscillatory. — When working with the arrangement shown in Fig. 3, it was noticed that the wire extending from *D* vibrated rapidly. It has already been found that the current through the mercury arc has rhythmic variations. A telephone was therefore connected directly between *C* and *D*. This gave a very distinct tone. The current through the arc was then passed through the primary of an induction coil and the secondary was connected to the telephone. This gave the same tone that had been produced when the telephone was connected between *C* and *D*. These experiments were tried with the current from a storage battery, in order that the fluctuations of the dynamo might be eliminated.

It was thought that possibly this rapid variation of the current through the arc might be aiding in the ionization of the gas, and an attempt was therefore made to get rid of these variations. The tube shown in Fig. 2 was used. Tin-foil was wrapped around the tube between *EF* and the main tube and *C* and *D* were connected to this foil, and this was then connected to the ground, but as far as could be detected this arrangement made no difference with the humming in the telephone. It certainly made no appreciable difference whether the tin-foil was connected to the ground, or left insulated. This experiment, therefore, showed nothing, except that it is very difficult to get rid of the effect due to the fluctuation of the current.

The effect could, however, be entirely stopped by connecting *C* and *D* by wire outside of the tube, showing that the humming was

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produced by an E.M.F. within the tube and not by a magnetic induction outside of it.

Summary. — The following facts have been brought out by this investigation. The space in the tube connected with a mercury arc becomes highly conductive. A luminous space gradually spreads out from the arc and the front of this region has the greatest luminosity and the highest conductivity. This conductivity is not due to ions coming from the arc, nor to rays sent out by it. It is not due to any leakage over the surface of the glass. It is probably not due to the high temperature of the gas. A probable explanation is that when ions first recombine, they are in a condition of unstable equilibrium much like the atoms of radio-active matter, and often break up again, this being a form of ionization which has not heretofore been studied.

There is an E.M.F. between electrodes inserted in different parts of the tube. This is possibly due to the more rapid diffusion of the negative ions.

Aid was received from the Carnegie Institution in purchasing the apparatus used in this work, and I desire at this time to express my thanks to the Institution for the grant.

COLGATE UNIVERSITY, October, 1905.

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THE ELECTRICAL PRODUCTION OF OZONE.

BY ARTHUR W. EWELL.

OZONE is produced by certain chemical reactions, by ultra violet light, by the electrolysis of certain solutions and (the most efficient method) by the extensive, continuous conduction of electricity through oxygen or air. Sparks produce little ozone and rapidly decompose any ozone already present. A gas exhibits this extensive conductivity (*i. e.*, is conducting throughout a large volume) if, either one of the electrodes, to which a high potential is applied, possesses sharp points or if an alternating current is employed and the electrodes are separated by the gas and a dielectric such as glass. Professor Warburg and the writer have quite exhaustively studied the production of ozone with the first type of ozonizer.[1] The maximum yield of ozone per coulomb was about 0.1 gr. With atmospheric air and the point electrode positive, the best yield in grams per kilowatt hour was about 27 and with an alternating current, or points negative, about 13. The temperature and pressure of the gas were found to be of small importance if the density remained unchanged, a result applicable to any method of ozonization.

A. W. Gray has studied one form of the second type of ozonizer, the dialectric being glass.[2] He found that the yield of ozone increased with the potential, and for the highest potential (12,240 volts for .062 cm. of oxygen and .168 cm. of glass) the yield was .225 gr. per coulomb. Neither the dialectric, nor the form of the electrodes nor their distance apart could be varied. No conclusive experiments were made with different gas velocities or ozone densities and the ozone density was very low.

Moreover a commercial alternating current was not employed. Dr. Gray used successive charges and discharges of a large con-

[1] Annalen der Physik, 17, 1905, p. 1.
[2] PHYS. REV., CIV., Nov., 1904, p. 347.

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denser, periodically charged by an influence machine. The great discrepancy between the yields of ozone with the two types of ozonizer, and the enormous discrepancies in the claimed efficiency of the different commercial modifications of the two general types [1] led the writer to undertake a study of the production of ozone with other electrodes than the point and plate which had already been so carefully studied.

Apparatus. — The final form of apparatus will be described. It is diagrammatically sketched in Fig. 1. The air is dried by passing through calcium chloride and concentrated sulphuric acid. A tube containing glass wool caught any bubbles of acid. The air then

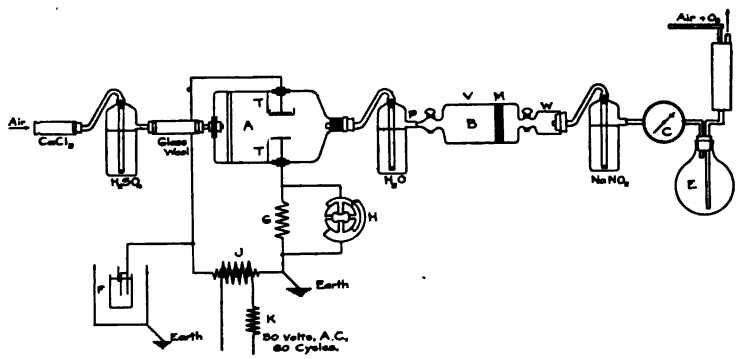

Fig. 1. Schematic Figure of Apparatus. *A*, ozonizer; *B*, sample tube; *C*, gasometer; *D*, Geryk pump; *E*, reservoir; *F*, repulsion voltmeter; *G*, non-inductive resistance; *H*, Dolezalek electrometer; *J*, transformer; *K*, rheostat.

entered the ozonizer. This was a four-liter bottle in which the electrodes (one form of which is illustrated) were mounted upon brass rods which passed through holes in the sides and were secured by nuts and asbestos washers. The bottom of the bottle had been carefully cracked off to give access to the interior, and when replaced and sealed with adhesive paper strip was secure and gas-tight. A brass tube with nuts and asbestos washers passed through the bottom and a glass tube passed through a rubber stopper in the neck. This stopper was protected from the ozone by paraffin and asbestos. Glass shields, *T*, *T*, confined the gas current to the space between the electrodes. Leakage over the glass surface was neg-

[1] For description of commercial ozonizers, etc., see article by the writer in Electric World for August 12, 1905.

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ligible, for the current was infinitesimal until the potential was sufficient to make the air conducting and then rapidly increased with increasing E.M.F. (see Fig. 4).

The ozonized air bubbled through fresh distilled water to absorb any nitrous oxide[1] produced with the ozone and then traversed in succession the sampling tube, sodium nitrite, to absorb the ozone, a gasometer, a ten-liter reservoir and the (Geryk) pump.

The three bottles were gas-washing bottles, in the necks of which fitted, with ground glass joints, the tubes figured, the lower ends of which were closed except for a circle of small holes near the bottom. At the joint marked *P*, one glass tube loosely fitted over the other, the joint being made tight by a ring of fine bleached cotton.

The main part, *V*, of the final sample tube had a volume of 680 c.c. A rubber stopper made connection between the funnel-shaped part, *W* (capacity = 60 c.c.), and the figured glass tube. The tube could be taken apart for cleaning at the ground-glass joint *M*.

An alternating current of 60 cycles was employed throughout all the experiments. The transformer was one limb of one designed by Prof. H. B. Smith. Its capacity was 100 k.w. and at full capacity its secondary e.m.f. was 500,000 volts. One side was grounded and the potential of the other side was determined by a mirror repulsion voltmeter. The latter was calibrated by measuring with calibrated Kelvin and Braun electrostatic electrometers the voltage across successive groups of windings of the secondary on open circuit and summing up. A calibration curve is given in Fig. 2. The current was determined by measuring with an idiostatic Dolezalek electrometer the fall of potential across a non-inductive resistance. For calibration, known alternating currents of the same frequency were employed. The calibration changed somewhat. The curve for July 5 is given in Fig. 2.

An experiment was conducted as follows: When the current and potential were satisfactory the air current was maintained for at least five minutes at the desired speed, as indicated by the gasometer readings per minute. Then the nearer cock of the sample tube was closed and immediately after, the farther cock. The sample tube was then disconnected and 50 c.c. of a solution of potassium

[1] Warburg, Annalen der Physik, 17, 1905, pp. 22.

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iodide (10 g. JK. in 500 c.c. H_2O) was poured into *W*. By opening the upper cock this was introduced into *V* and thoroughly shaken with the ozonized air. The amount of ozone could be roughly judged by the yellow color due to the liberated iodine. The solution was then drawn out, an equivalent amount of sulphuric acid added and adding starch, was titrated with a one-fiftieth normal

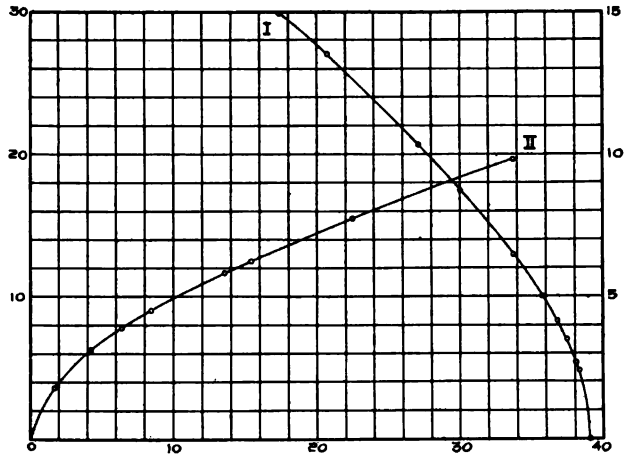

Fig. 2. I., Calibration of repulsion voltmeter for July 12. II., Calibration of Dolezalek electrometer for July 5. For I.: Abscissæ = scale reading (cm.) on scale 1 m. from mirror. Ordinates = kilo-volts (scale on left). For II.: Abscissæ = deflection (cm.) on scale 1 m. from mirror. Ordinates = volts (scale on right).

solution of sodium thio-sulphate. Readings could be made to 0.01 c.c. = .0048 mg. ozone. If recoloration of the titrated solution occurred within two hours the experiment was discarded. Professor Warburg has shown that absence of such recoloration within two hours proves that practically no nitrous oxide was present.[1]

Point and Plate Electrodes. — As a test of the apparatus the first experiments were with one plane electrode 13 cm. by 5 cm., and the other electrode having 90 pin points distributed over an equal area. Under the best conditions the yield was about 12 gr. per kilowatt hour (at the electrodes) and .04 gr. per coulomb. The current varied from 300 to 2,000 micro-amperes. As the distance

[1] Annalen der Physik, 17, 1905, p. 22. With the second type of ozonizer, the type employed in most of the experiments described in this paper, the production of nitrous oxide is much less than with a point electrode. Apparently, the more diffuse the discharge the less the production of nitrous oxide.

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between the electrodes was increased the maximum current decreased, the yield per coulomb increased and per kilowatt hour decreased. In general the results obtained showed good agreement with the experiments conducted in Professor Warburg's laboratory and therefore the apparatus and methods were considered satisfactory.

Point and Point Electrodes. — Two point electrodes similar to the one above gave a very low relative efficiency, sparks occurring more readily than with point and plate electrodes. Experiment 88 of July 27 is typical.

Distance between electrodes = 2.0 cm. Gas velocity = 3 l. per min.
Current (micro-amperes) = 1,300. Dif. of Pot. = 1,500.
Yield per coulomb = .003; per kilowatt hr. = 1.1.

Plate and Plate Electrodes. — A very inefficient system, as sparks occur before the desired brush discharge is appreciable.

Gauze and Plate Electrodes. — Various copper and brass gauzes with meshes varying from 40 to 1,600 per sq. in. were tried, the edges of the electrodes being carefully turned in to avoid points. The maximum current before sparking was very low and so also was the yield of ozone. The same results were found with both electrodes gauzes.[1]

Both Electrode Plates, one bare, the other covered with a Dielectric. — The electrodes were tin plates 7.3 cm. in diameter, one covered with a glass crystallizing dish with 4 cm. sides (see Fig. 1).

Variation of Gas Velocity. — Since the yield varies also with the current observations are made with each gas velocity throughout the range of the current. The results are given in table I. Every attempted experiment was numbered and omitted numbers belonged to incomplete or unreliable experiments. *The gas velocity v is in liters per min. The potential V, in volts, the current i in micro-amperes, the mass of ozone, m, is the actual number of milligrams per minute. the yield Y_1, the number of grams per coulomb and Y_2 the number of grams per kilowatt hour. Y_2 is less than the true yield per kilowatt hour* for the power factor was never one and probably much less than one for the shorter distances. The writer hopes shortly to determine the value of the power factor under the various conditions of these experiments.

[1] Contrary to the results of Rosenberg (Elec. Rev. (London), 55, p. 807), but see Electric World, Aug. 12, 1905, p. 267.

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TABLE I.

Distance between Electrodes $= d_1 = 1.00$ *cm.; between bare Electrode and Glass* $= d_2 =$ .65 *cm.; Thickness of Glass* $= .2$ *cm.*

No.	v	V	i	m	Y_1	Y_2
52	4.5	14,700	1,100	1.26	.019	4.7
53	4.5	13,200	480	2.32	.081	24.0
54	4.5	12,000	270	2.4	.123	36.0
56	4.5	10,400	44	0	0	0
60	2.4	12,200	117	.30	.043	12.0
61	2.4	12,600	210	.92	.073	20.0
62	2.4	15,800	2,000	.96	.008	1.8
63	12.0	11,200	143	.22	.026	7.7
64	13.9	15,600	1,960	9.1	.077	17.0
65	13.9	13,100	500	3.5	.12	32.0
67	2.2	12,200	515	.71	.023	6.8
68	12.0	11,600	270	3.1	.18	57.0
69	12.9	11,600	220	1.85	.14	45.0
70	12.9	12,200	360	4.3	.20	60.0
71	4.5	12,000	158	.90	.095	29.0

The relations between yields per coulombs Y_1, current i, and gas velocity v are plotted in Fig. 3. The curves show conspicuously

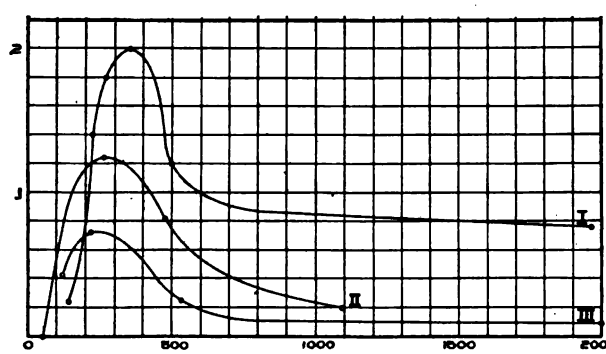

Fig. 3. Abscissæ = Micro-amperes. Ordinates = Grams per coulomb. Polar Distance = 1.0 cm. I., 13 liters of air per minute; II., 4.5 liters of air per minute; III., 2.4 liters of air per minute.

that the greater the current, the greater both the ozonizing power of the current and its deozonizing effect on the ozone already formed resulting in the maxima of the curves. The greater the gas velocity, the greater the maximum yield and the current at which this maximum occurs, and the greater the ozone density or the mass of ozone

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per liter. (The latter is evident upon comparison of the second and fifth columns.) It is therefore evident that *for greatest efficiency a high gas velocity must be used.*

Upon plotting potential horizontally and current vertically the rapid increase of current at a certain potential is very evident (Fig. 4). At this point where the current commences to rapidly increase with the potential, the discharge begins to be both visible and audible and the production of ozone commences. Fig. 4 also proves

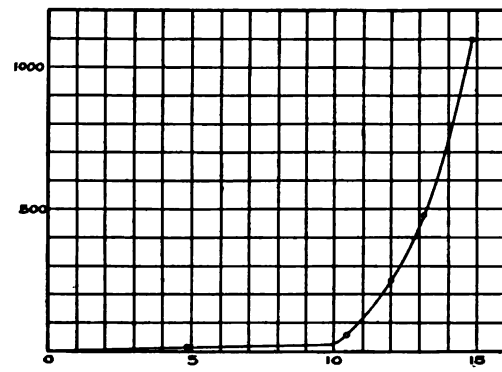

Fig. 4 Abscissæ = Kilo-volts. Ordinates = Micro-amperes. Polar Distance = 1.0 cm. Thickness of glass = .2 cm. 4.5 liters of gas per minute.

the small amount of leakage over the glass surface and the relatively small "condenser" current in the gas.

Variation of Distance.— Gas velocity = constant = 12 l. per min. One electrode = bare tin plate 7.3 cm. in diameter, the other a similar disc of tin foil cemented inside a crystallizing dish.

TABLE II.

d_1 = Distance between Electrodes = .60; d_2 = Distance between bare Electrode and Glass = .45.

No.	V	i	m	Y_1	Y_2
72	14,500	2,360	8.1	.057	14
73	14,300	2,280	8.8	.064	16
74	9,500	1,060	8.9	.14	44
75	7,300	300	1.8	.10	50
76	8,200	830	5.7	.115	55
77	6,200	560	3.7	.109	63
78	10,200	1,200	15.0	.208	73
79	11,800	1,720	13.8	.132	40
80	10,600	1,380	14.2	.173	58

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TABLE III.

$d_1 = 3.20$; $d_2 = 3.05$.

No.	V	i	m	Y_1	Y_2
81	26,200	1,840	5.3	.048	6.6
83	23,800	680	4.8	.118	18.0
84	23,200	310	2.9	.16	25.0
85	22,400	180	2.6	.24	38.0
86	18,400	49	0	0	0

The results are plotted in Fig. 5. With the greater distance the air current was wider and consequently the speed of the air particles less, the volume gas velocity being the same — 12 liters per min.

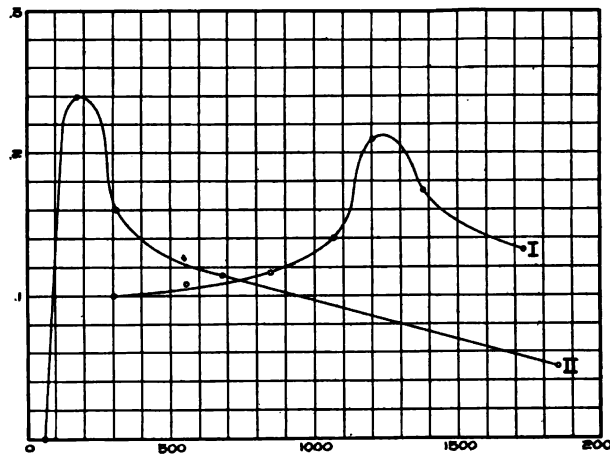

Fig. 5. Abscissæ = Micro-amperes. Ordinates = Grams of ozone per coulomb. Liters of gas per minute = 12. I., Polar Distance = .6 cm.; II., Polar Distance = 3.2 cm.

The ozone formed was therefore longer exposed to the deozonizing effect of the current and the maximum yield comes at a lower current.

Experiment 78, which represented approximately the best conditions, will be described in full.

July 17. Temp. = 27°. Bar. = 75.2. Sultry.

Sample tube = 640 c.c. Gas velocity = 12 l. per min.

$d_1 = .60$. $d_2 = .45$.

Repulsion voltmeter = 35.8 (zero = 39.4); from calibration of that day = 10,200 volts.

Dolezalek electrometer = 10.6 (zero = — 5.0) = 6.0 volts.

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Non-inductive resistance = 5,000 ∴ i = 1,200 micro-amperes.

$Na_2S_2O_3$ titration = 1.66 c.c. = .80 mg. O_3.

O_3 per min. = .80 × 12 ÷ .64 = 15 mg. Coulombs per min = .072. Watts = 12.2.

Yield per coulomb = .208.

Yield per kilowatt hr. = 73.

Ozone density = 1.39 gr. per cubic meter.

The above results show that if the amount of gas which flows between the electrodes is the same, the maximum yield of ozone per coulomb is approximately independent of the distance between the electrodes, but that if the distance is decreased, the current at which this maximum occurs is greater, and hence the ozone density is greater and a small distance is preferable. Would the shorter distance also be preferable if the actual velocity of the air particles was the same? A large number of experiments were made with different distances, the gas space and the volume gas velocity being adjusted so that the average velocity of the air molecules was approximately the same. The modified apparatus was not entirely satisfactory and the results were not as reliable and consistent as in the rest of the work and will not be given in detail. The results indicated that with equal velocities of the gas particles the maximum yield per coulomb was greater for the greater distance, but increased at a considerably less rate than the distance. The current for which the maximum yield occurred at the greater distance was nearly equal to the corresponding value of the current for the less distance. These results can also be deduced from a study of Figs. 3 and 5.

Effect of Width of Electrodes. — One electrode = bare tin plate 7.0 × 1.4 cm.

Other electrode = tin foil strip 7.0 × 1.4 cm. inside crystallizing dish.

d_1 = .95. d_2 = .80 cm. Gas velocity = 12 l. per min.

TABLE IV.

Greater Dimension of Electrodes Perpendicular to Gas Current.

No.	V	i	m	Y_1	Y_2
157	21,500	1,060	6.3	.10	17
159	17,500	660	7.3	.35	72
161	20,200	800	18.7	.39	70
162	22,500	980	15.3	.26	41
163	16,000	500	6.3	.21	47

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TABLE V.

Greater Dimension Lengthwise to Gas Stream.

No.	V	i	m	Y_1	Y_2
164	22,500	1,060	4.1	.065	10
165	20,000	810	7.4	.15	27
166	17,300	590	5.3	.15	31
167	18,000	670	6.4	.16	32

These results are plotted in Fig. 6. *Narrow electrodes are evidently much more efficient*, a result expected since the ozone formed

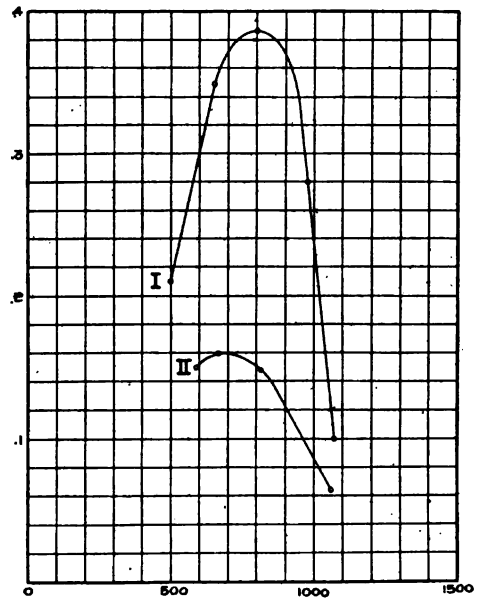

Fig. 6. Abscissæ = Micro-amperes. Ordinates = Grams per coulomb. Polar distance = .95 cm. 12 liters of air per minute. Electrodes 7.0 cm. by 1.4 cm. I., Longer dimension perpendicular to air stream. II., Longer dimensions parallel to air stream.

is exposed for less time to the current's deozonizing influence.

Influence of Dielectric. — One electrode bare, the other covered with one crystallizing dish.

$d_1 = .95$, $d_2 = .80$. Gas velocity = 12 l. per min.

TABLE VI.

No.	V	i	m	Y_1	Y_2
132	16,800	920	15.2	.28	61
133	15,900	780	17.4	.37	84
134	15,100	700	13.4	.32	76
136	14,000	600	9.3	.26	67

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Experiment 133 will be given in full.

August 9. Temp. = 24°, Bar. = 75.8.

Sample tube = 680 c.c. Gas velocity = 12 l. per min. $d_1 = .95$. $d_2 = .80$.

Repulsion voltmeter = 30.9 (zero = 39) = 15,900 volts.

Dolezalek electrometer = 21.7 (zero = — 6.8) = 7.8 volts.

Non-inductive resistance = 10,000 ohms, hence $i = 780$ micro-amperes.

$Na_2S_2O_3$ titration = 2.06 c.c. = .99 mg. ozone.

Ozone per minute = .99 × 12 ÷ .68 = 17.5 mg.

Coulombs per minute = .047. Yield per coulomb = .37.

Watts = 12.4. Yield per kilowatt hour = 84.

Ozone density = 1.46 gr. per cubic meter.

One electrode plain, the other covered with two crystallizing dishes.

$d_1 = 1.2$. $d_2 = .80$. Gas velocity = 12 l. per min.

TABLE VII.

No.	V	i	m	Y_1	Y_2
122	17,500	450	5.7	.21	44
123	19,200	660	9.9	.25	47
124	21,400	860	21.2	.41	68
126	22,800	1,020	12.8	.21	33
128	21,500	840	16.6	.31	52
129	23,400	1,120	12.1	.18	28
130	19,400	690	12.4	.30	56
131	20,400	790	20.9	.44	65

Both Electrodes Covered with Glass. — Both electrodes consist of tin foil on the inside of glass crystallizing dishes.

$d_1 = 1.0$, $d_2 = .85$. Gas vel. = 12 l. per min.

TABLE VIII.

No.	V	i	m	Y_1	Y_2
95	28,000	1,280	11.2	.13	17
98	13,700	232	1.8	.13	35
99	19,700	590	5.6	.16	29
100	24,000	820	7.9	.16	24
101	18,000	440	3.6	.14	28
103	30,200	1,240	11.2	.15	18
104	22,600	680	5.8	.14	22
107	31,400	1,100	11.8	.18	21
108	26,000	870	8.3	.16	22

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The relations between yield per coulomb and current are plotted in Fig. 7.

Comparing these different results, it is evident that the thickness (and hence the nature) of the dielectric has practically no influence on the yield per coulomb but that if both are covered with dielectric the yield per coulomb is less (and the apparent resistance is greater). Also, the less the dielectric the lower the required

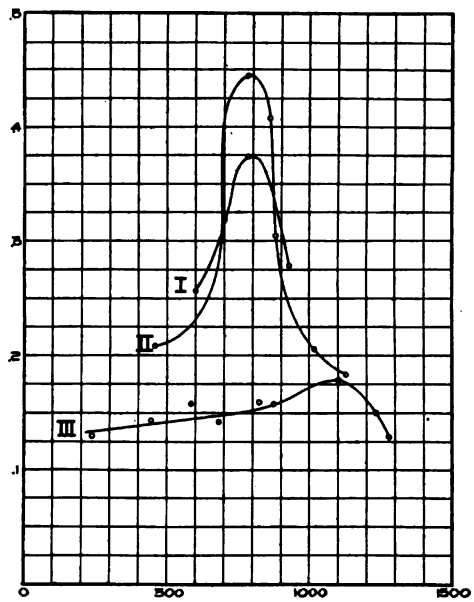

Fig. 7. Abscissæ = Micro-amperes. Ordinates = Grams per coulomb. Polar distance = about 1 cm. 12 liters of air per minute. I., One electrode bare, the other covered with single glass. II., One electrode bare, the other covered with double glass. III., Both electrodes covered with glass.

potential and the greater the yield per kilowatt hour. Therefore *for greatest commercial efficiency*, there should be a *thin dielectric of high dielectric strength in the gas space between the electrodes.*

When the potential is sufficient to make the air conducting, the air is most luminous near the electrodes. Professor Warburg[1] has shown that with point and plate electrodes, luminosity and the production of ozone are very intimately connected. It is, therefore, natural that we find more ozone produced near the electrodes in this type of ozonizer.

[1] Ann. der Physik, 17, 1985, p. 1.

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Comparing the best yield per kilowatt hour with point and plate electrodes, 27 grams with points positive and 13 grams with points negative or alternating, *with the yield of over 70 under the best conditions with alternating current and the electrodes separated by a dielectric* (see Tables II., IV. and VI.) *it is evident that the latter system is by far the more efficient.* The actual yield is considerably over 70 since the power factor has been assumed as unity.

Conclusions. — These experiments upon the electrical production of ozone have chiefly shown three things; first, the superiority of the silent discharge obtained with an alternating current and the interposition of dielectric between the electrodes, over that obtained with a point electrode; second, the marked deozonizing effect of the current and how to reduce this influence, and third, the ideal dielectric.[1]

I wish to thank Professor Warburg for the hospitality of his private laboratory where I began the study of the electrical production of ozone under his guidance and Prof. H. B. Smith for very kindly placing at my service the high potential apparatus of the Department of Electrical Engineering, of the Worcester Polytechnic Institute.

SALISBURY LABORATORIES,
WORCESTER POLYTECHNIC INSTITUTE,
WORCESTER, December, 1905.

[1] [An ozonizer has been constructed embodying the results of these experiments and in preliminary trials shows very high efficiency. The electrodes are straight, parallel, nickel-plated wires, all in the same plane, alternate wires projecting on each side and being joined to the external electrode. Perpendicular to the plane of the wires and *midway between each pair of wires* is a flat plate of dielectric, sufficiently wide to prevent direct discharge between the wires. The shape of the dielectric being the simplest possible, the danger from breakage is a minimum and the choice of dielectrics is greatly increased. Glass and fiber have proved very satisfactory. Hard rubber is apparently acted upon by the ozone and mica gives an irregular discharge. March, 1906.]

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PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE THIRTY-FIRST MEETING.

A REGULAR meeting of the Physical Society was held in Fayerweather Hall, Columbia University, New York City, on Saturday, February 24, 1906. President Barus presided.

On motion the president, the secretary and E. B. Rosa were made a committee to prepare a memorial to Congress urging the passage of the pending bill which provides for the use of the metric system in all the government departments.

On motion a committee was appointed consisting of A. G. Webster (chairman), M. I. Pupin and P. C. Hewitt, to consider the practicability of securing for the Physical Society an endowment fund, the income of which shall be available to meet the expenses of committees appointed by the Society to investigate and report on special topics of importance.

The following papers were read:

1. A Direct-Recording Magnetic Declinometer. W. G. CADY.
2. A Machine for Compounding Sine Curves. W. G. CADY.
3. The Damping of a Ballistic Galvanometer. (Read by title.) A. W. SMITH.
4. Further Experiments on the Decay of Phosphorescence in Sidot Blende. E. L. NICHOLS and ERNEST MERRITT.
5. The Decay of Phosphorescence in a Certain Specimen of Willemite. E. L. NICHOLS and ERNEST MERRITT.
6. The Gray Absolute Electrodynamometer. E. B. ROSA.
7. On the Relative Proportion of the Total X-ray Activity of Radioactive Minerals due to the Separate Radioactive Constituents. B. B. BOLTWOOD.
8. The Radioactivity of Thorium. H. M. DADOURIAN.
9. Nucleation and Ionization in CO_2 and Coal Gas. CARL BARUS.
10. Temperature Records of Nocturnal Radiation. H. T. BARNES.
11. On the Possible Separation of Electric Charges by Centrifugal Accelerations. E. F. NICHOLS.

The spring meeting of the society will be held in Washington.

ERNEST MERRITT,
Secretary.

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TREASURER'S REPORT FOR THE YEAR 1905.

RECEIPTS.

Balance from 1904	$1,625.12	
Interest on balance	56.88	
Arrears of dues	15.00	
Life membership fees, three	150.00	
Initiation fees, twenty	60.00	
Refund on Nomenclature Committee	17.60	
Annual dues for 1905	1,295.00	$3,219.60

DISBURSEMENTS.

Physical Review, 247	$ 741.00	
Science abstracts, 284	426.00	
Andrus and Church, Printing, etc.	128.00	
Office of Secretary	142.40	
Office of Treasurer	21.40	
Drafts and collections	3.50	
Incidental printing	14.47	$1,477.07
Balance carried to 1906		1,742.53
		$3,219.60
Total annual outlay		$1,477.07
Interest on fund	$ 56.88	
Annual dues	1,295.00	
	1.351.88	
APPARENT DEFICIT	125.19	1,477.07

THERMOELECTRIC HETEROGENEITY IN CERTAIN ALLOYS, ESPECIALLY GERMAN-SILVER.[1]

BY EDWIN H. HALL, L L. CAMPBELL AND S. B. SERVISS.

IN calibrating thermo-electric couples made of annealed german-silver with copper for the temperature region 100° to 218°, using a temperature interval not far from 40°, the authors found the electromotive force, in the case of some couples, to vary as much as two or three per cent. of itself when the junction which had been the hotter became the colder and *vice versa*. The german-silver wires were about 0.02 cm. in diameter and about 150 cm. long. A part some 45 cm. long near the middle of each german-silver wire was, in these experiments, outside the heating vessels, and at first no care was taken to keep this part warm, so that steep gradients of temperature existed in the german-silver wire just outside the entrance to each vessel. It was at first thought that local peculiarities of this wire due to accidental bending or stretching after the an-

[1] Abstract of a paper presented at the meeting of the Physical Society held on Dec. 29–30, 1905.

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nealing might, if these peculiarities happened to come at places where the temperature gradient was steep, cause the changes observed on reversal of the temperature interval of the junctions. Experiment seemed to show, however, that these peculiarities could not reasonably be made to account for all of the difference of electromotive force observed on this reversal.

Further experiments, made by touching with the sharp edge of a lump of ice various points 1 cm. apart on long straight pieces of german-silver wire exposed to air at a temperature of 18° or 20° centigrade, gave perceptible electromotive forces, some of which were in one direction and some in the other direction, about twenty changes of sign occurring in a distance of 50 cm. along the wire. Annealing a wire, by heating to incandescence for a few seconds in air, was found to increase its thermo-electric heterogeneity. Permanent stretching of a wire 10 per cent. left the local thermo-electric peculiarities almost unchanged in magnitude and in distribution. Reannealing a wire after such a stretching again increased these local peculiarities and changed their distribution. The greatest electromotive force observed on touching a german-silver wire with ice was about $\frac{1}{500}$ part of that which would have been produced by touching a junction of copper and german-silver. The heterogeneity thus found in straight recently annealed wire is great enough to be a possible source of serious error in cases where a copper-german-silver couple is used to measure a small difference between two temperatures much above the temperature of the room, if the middle part of the german-silver wire is freely exposed to the air. In later calibration experiments the difference of electromotive force found on reversal of the temperature interval of the junctions was greatly diminished by protecting the middle parts of the german-silver wires with asbestos fiber, so that, being near the heating vessels, they were raised to a temperature not far below that of the cooler vessel.

A manganin wire, tested by touching at various points with ice, behaved very much as german-silver wire did. A constantin wire showed local differences, but these were much less than in german-silver or in manganin.

The Optical Properties of Carbon.[1]

By Herbert A. Clark.

An anomaly in the dispersion and in the absorbing and radiating powers of carbon has been found by Wood and E. L. Nichols. In view of this fact, it has seemed worth while to obtain data regarding the reflection as well as the absorption and dispersion, all from the same specimen, of carbon deposited in various ways.

[1] Abstract of a paper presented at the meeting of the Physical Society held on Dec. 29–30, 1905.

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In this work, transparent films were used, some deposited in vacuo and some on the inside of an electric lamp globe. Of the former, the reflection, refraction, and transmission were obtained quantitatively throughout the visible spectrum; and the transmission qualitatively in the ultraviolet. Of the latter films, the transmission and the direction of the refractive index curve were obtained in the visible spectrum. As is to be expected from the observations of others upon the electrical properties of thin films, the optical properties vary markedly with the manner and conditions of deposit.

METHODS OF SOIL HYGROMETRY.[1]

BY E. BUCKINGHAM.

AFTER a brief mention of the importance in agricultural investigations of having a good method for determining the water content of the soil at any given depth, and a statement of the merits and defects of the gravimetric and electrolytic methods now in use, the paper goes on to state the general principles on which any successful method must be based.

It is necessary to select some physical property of the soil which may be conveniently and accurately measured without disturbing the soil; and the property must be such that to every measured value of this property there corresponds one and only one value of the water content of the soil. The property must vary sufficiently with the water content of the soil, and must not depend on the variable concentration of the substances dissolved in the soil moisture.

The index of refraction for short electrical waves appears to satisfy these requirements reasonably well. Experiments by L. J. Briggs and the writer, using Drude's method, with the soil in the end condenser and a wave-length of from 50 cm. to 200 cm., showed that the specific inductive capacity of the soil does vary sufficiently with the water content and is independent of the concentration of the soil solution, up to such concentrations as occur under natural conditions in the soil. Further experiments were made similar to Hertz's original experiment with the wire rectangle,[2] and to the experiments of Rubens and Arons.[3] Waves from an oscillator enter a divided circuit and, after traversing the two arms, meet at a spark micrometer where the sparking is a minimum if the same time is required for the waves to traverse each arm. If one

[1] Abstract of a paper presented at the meeting of the Physical Society held on Dec. 29–30, 1905.

[2] Wied. Ann. 31, 421, 1887.

[3] Wied. Ann. 42, 581; 44, 206. 1891.

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arm of the circuit is led through the ground, the point at which the waves must be introduced in order to give a minimum of sparking at the spark micrometer, varies with the wetness of the soil, and by gravimetric calibration the readings of the instrument may be interpreted in terms of the percentage of water in the soil surrounding the soil arm of the circuit. It is hoped to extend these experiments, which only have a preliminary character, and to develop on these lines a practical method of soil hygrometry. Diagrams of the instrumental arrangements were shown, together with a graphical representation of results obtained during June, 1905, in the loam soil of a flower bed.

A Direct-Recording Magnetic Declinometer.[1]

By W. G. Cady.

A PRELIMINARY paper on this instrument was published in *Terrestrial Magnetism* for June, 1904. Since then one declinometer of this type has been constructed at Wesleyan for the Dept. of Terr. Mag. of the Carnegie Institution and sent to the Solar Observatory at Mt. Wilson, Cal. A second instrument, also intended for the Carnegie Institution, is now nearing completion.

The motion of a magnetic needle is transmitted through a delicate suspended lever to a glass pen, which prints a dot once a minute on a strip of paper. The paper is advanced and the printing accomplished automatically by means of clockwork. Also, if the magnet changes its direction by more than a prescribed amount, an electric alarm rings. Due allowance is here made for the normal course of diurnal variation.

A fixed pen traces a base-line near one edge of the paper. To determine the sensitiveness, a telescope, scale, and deflecting magnet are provided. The sensitiveness can be varied at will; good records are obtained with the scale-value as small as 1.5 minutes of arc per millimeter.

A Machine for Compounding Sine Curves.[1]

By W. G. Cady.

A PENCIL moved up and down by a train of gear wheels pressed against a vertical sheet of paper, which is drawn along horizontally by means of a rack and pinion. The same shaft that turns the wheels also advances the paper. By means of reduction gearing and various

[1] Abstract of a paper presented at the meeting of the Physical Society held on Feb. 24, 1906.

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adjustments, a fundamental sine curve with a period of 48 cm. can be drawn alone, or compounded with its second, third or fifth harmonic, any desired amplitude and phase relations being possible. The machine itself was shown, together with various sample curves.

DAMPING OF A BALLISTIC GALVANOMETER.

BY ARTHUR W. SMITH.

THE equation of the ballistic galvanometer is

$$Q = \frac{H}{G}\frac{T}{\pi}\theta = \frac{H}{G}\frac{T}{\pi}\theta_1\left(1 + \frac{\lambda}{2}\right),$$

where θ denotes the virtual deflection which would be obtained if there were no damping. The actual deflection, θ_1, is less than θ, the familiar relation being $\theta = \theta_1(1 + \lambda/2 +)$. λ is the logarithmic decrement, *i. e.*, the natural logarithm of the ratio of one amplitude to the next.

A more simple method of determining the damping factor is the following: For brevity let k denote this factor. By definition, $\theta = k\theta_1$. Similarly $\theta_1 = k\theta_2$, where θ_2 is the virtual deflection at the end of the second half amplitude and when the needle is passing its position of rest.

In other words, θ_2 is the deflection which would be obtained if damping should suddenly cease at the end of the second half amplitude. The actual deflection, θ_3, is less than this, or $\theta_2 = k\theta_3$. In the same way, $\theta_3 = k\theta_4$ and $\theta_4 = k\theta_5$, θ_5 being the next deflection in the same direction as θ_1. Hence $\theta_1 = k^4\theta_5$, and $\theta = (\theta_1/\theta_5)^{\frac{1}{4}}\theta_1$. The complete equation then becomes

$$Q = \frac{H}{G}\frac{T}{\pi}\theta_1\left(\frac{\theta_1}{\theta_5}\right)^{\frac{1}{4}},$$

which is much more simple and direct than the usual method of considering the "logarithmic decrement" and obtaining k in the form of an infinite series.

TEMPERATURE RECORDS OF NOCTURNAL RADIATION.[1]

BY H. T. BARNES.

ON account of the great cold of the Canadian winter together with the extreme dryness of the atmosphere it was considered of interest to obtain some record of the copious radiation that takes place from the surface into space during the night time.

[1] Abstract of a paper presented at the meeting of the Physical Society held on Feb. 24, 1906.

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Until more satisfactory apparatus could be obtained for permanently carrying out the work, the electric recorder was used, which is in use at the McGill College Observatory for giving the difference in temperature at different altitudes, and which was described at the last meeting of the Physical Society by Professor McLeod and the author.

The high level thermometer was brought down and connected in the circuit at the observatory beside the low level instrument, and temperature traces taken on several clear nights with one thermometer exposed to the sky and the other under cover.

A considerable divergence from the zero line was obtained which varied with the clearness of the atmosphere.

At the present time a special recorder is being fitted up with special thermometers and it is the author's intention to continue the work for the rest of the winter, and at the same time to obtain if possible the absorptive power of some materials for the long heat waves radiated from the earth at a low temperature.

That the radiation is considerable, is shown by the abundant formation of anchor or ground ice at the bottom of quite deep rivers and streams which are flowing too swiftly to allow surface ice to form. This ice is dependent on the clearness of the sky and never forms under surface ice.

McDonald Physics Building,
McGill University, February 19, 1906.

The Radio-activity of Thorium.[1]

By H. M. Dadourian.

It has been claimed by several experimenters that the radio-activity of different preparations of thorium is not the same, in fact, that it is possible to obtain, from certain sources, thorium which is entirely inactive.

In view of these facts and of the doubts which have been raised as to the elementary character of thorium it was deemed desirable to determine the quantitative relation between the thorium activity of various minerals and separated salts, and their content of thorium.

The method used was based upon the measurement of the activity of the material deposited upon a cathode exposed to the emanation from solutions of these minerals and salts. The slower decay of the deposit due to the thorium emanation made it possible to separate it from the deposits due to radium and actinium. The method proved to be capable of giving accurate quantitative results.

[1] Abstract of a paper presented at the meeting of the Physical Society held on Feb. 24, 1906.

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It was found that the thorium activity of thorite and thorianite taken as natural minerals was proportional to the amount of thorium contained in these minerals, while thorium nitrate from North Carolina and Brazilian monazites prepared by the Welsbach Light Company had a specific thorium activity only half as large.

To make this certain Dr. B. B. Boltwood, to whom the writer is indebted for all the minerals and salts used in these experiments, separated the thorium from a few grams of North Carolina monazite and converted it into a nitrate. The specific thorium activity of this preparation was found to be equal to the specific thorium activity of thorite and thorianite.

These results show that the radio-activity of thorium, and consequently the radio-thorium in a mineral, is proportional to the quantity of thorium present in the mineral, further, that radio-thorium is a disintegration product of thorium.

The fact that commercially prepared thorium salts have lower specific thorium activity leads to the conclusion that about half of the equilibrium quantity of radio-thorium is removed from these salts in the chemical process of their preparation.

The results of these experiments strongly indicate the elementary character of thorium itself.

In conclusion I wish to express my hearty thanks to Professor H. A. Bumstead for suggesting these experiments and for the interest he has shown during the progress of the work.

THE NUCLEATION AND IONIZATION OF CARBON DIOXIDE AND COAL GAS.[1]

BY CARL BARUS.

IN these experiments I have used the apparatus with which I obtained the data in case of dust-free air, for CO_2 and coal gas, finding the nucleation for these gases both in the non-energized and in a typically energized state. The results in both investigations are suggestive in character. CO_2 behaves in a way closely resembling air (energized or not), but in such a way that a given corona appears in CO_2 at a pressure difference about 5.5 cm. higher than in case of air. In other words the behavior is as if the nuclei of CO_2 were throughout smaller. It is to be noticed, however, that the heat ratio γ is smaller for CO_2 than for air which would in part account for this result.

Coal gas needs more detailed discussion, but behaves in general like CO_2.

[1] Abstract of a paper presented at the meeting of the Physical Society held on Feb. 24, 1906.

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NEW BOOKS.

Die Kathodenstrahlen. By G. C. SCHMIDT. 8vo, pp. vii + 120. Braunschweig, Vieweg und Sohn, 1904.

Electromagnetische Schwingungen und Wellen. By JOSEF RITTER VON GEITLER. 8vo, pp. viii + 154. Braunschweig, Vieweg und Sohn. 1905.

Die Physikalischen Eigenschaften der Seen. By OTTO FREIHERR VON UND ZU AUFSESS. 8vo, pp. x + 120. Braunschweig, Vieweg und Sohn, 1905.

These interesting and useful little books form part of a series of semi-popular monographs on scientific and mathematical subjects, the publication of which, under the general title "Die Wissenschaft," was begun two years ago. The place of honor as first of the series was given to a German translation of Madame Curie's dissertation on Radioactive Substances. The plan and purpose of the series are explained in the following extract from the publisher's announcement:

"It is becoming more difficult every year to follow the advances that are being made in the mathematical and natural sciences. It is true that numerous reference periodicals report the results of the more recent investigations with more or less promptness, but without systematizing and unifying these results. The progress made in the various branches of science can be readily followed, however, only when comprehensive résumés, each dealing with some special topic, appear at rather frequent intervals. Such résumés would serve also to give the specialist a glimpse into those fields of scientific activity which are related to his specialty. Considerations of this kind have led in France to the publication of the 'Scientia' series. In Germany the collection of monographs on scientific and mathematical subjects which is to appear under the title 'Die Wissenschaft' is intended to serve the same purpose. The treatment is not intended to be 'popular' in the ordinary sense in which the word is used, since not only the results of general interest will be presented, but also the experiments and the theoretical considerations which have led to the results. . . ."

It is scarcely to be expected that these monographs will be very generally read in this country outside of scientific circles, for the treatment is more thorough than is usual in our popular scientific books. But for those having the requisite knowledge of German, and who desire

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something more than the superficial accounts of scientific work that are so common with us, the collection will be quite welcome. For physicists who wish to keep track of the progress in branches related to their own, but who cannot spare the time needed for the consultation of the original articles, "Die Wissenschaft" collection will certainly be found extremely useful.

The monograph by Professor Schmidt on the Cathode Rays is a very readable and reasonably complete account of the development of this important subject down to the year 1904. Not only the ordinary cathode rays of the vacuum tube but also those developed in other ways are considered; for example the rays produced at the surface of an incandescent body by the action of ultra-violet light, and the β-rays of radium. The book also contains chapters on canal rays, the Zeeman effect, and apparent mass. The significance of the results in their bearing upon the electron theory is accentuated. A systematic arrangement of the material in chapters in part makes up for the unfortunate lack of an index, while references to original articles, although by no means complete, include the most important work up to the time of publication.

Numerous books of a popular and semi-popular character dealing with electric oscillations and electric waves have appeared in recent years, and have treated the subject in a variety of different ways. In some cases it is the experimental side of the subject that has been thrown into the foreground; in others especial prominence has been given to the bearing of the work of Hertz upon electrical and optical theories; while in many instances the purely scientific side of the subject has been subordinated to the applications of electric waves in wireless telegraphy. If only one book on the subject is to be read, it is probable that either one of several books that might be mentioned would be found more satisfactory than that of von Geitler. But for one wishing to go into the subject more thoroughly this little monograph will be found very useful. The treatment is often so brief as to be in itself quite inadequate. But on the other hand the book contains a large amount of material which it would be difficult to find elsewhere without an extended search of the literature, and the value of the book is greatly increased by the unusually complete references to original papers. As a book of reference especially it will take a position that has not before been adequately filled.

In the "Physical Properties of Lakes," by von Aufsess, we have an interesting presentation of an unusual subject. I think that the physicist often experiences a certain feeling of envy when he sees how readily the botanist or the mineralogist is able to combine a summer outing or an interesting journey with more or less serious scientific work. To some extent the physicist is able to do this also, as is evidenced by Tyndall's study of the Alpine glaciers, and by the work of Elster and Geitel

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on atmpospheric ionization. But such cases are not usual. The little book by Freiherr von Aufsess will give to the physicist who loves outdoor life an added interest in any lake that he may encounter in his travels, and will help to explain some of the phenomena that must have puzzled every one who has spent any time near a large body of water.

The book is divided into chapters according to the branch of physics in which the phenomena considered naturally fall: Mechanics, Sound, Light, and Heat. Personally the reviewer has found the most interesting chapters to be those dealing respectively with waves and with the color of lakes. The treatment is often not as complete as might be desired; in many cases the problems have doubtless not yet been fully solved. The book is not to be compared in interest with the writings of Tyndall on the Alps, since the narrative element is lacking; but it forms one of a class of books on physics whose number is as yet far too small.

ERNEST MERRITT.

Populäre Schriften. By LUDWIG BOLTZMANN. 8vo., pp. vii + 440. Leipzig, Barth, 1905.

Those who are familiar with the clear and pleasing style which Boltzmann can adopt when he enters the field of semipopular writing will welcome the appearance of this collection. It contains twenty-three addresses or magazine articles, dealing with a great variety of subjects, chiefly, however, such as are closely connected with physics. The following titles will give an indication of the nature of the topics considered: "Die Methoden der theoretischen Physik"; "Ueber Maxwell's Elektrizitätstheorie," especially interesting because of its original appearance, in 1873, before the theory had reached its present secure position; "Der Zweite Hauptsatz der Mechanischen Wärmetheorie"; "Ueber Luftschiffahrt"; "Josef Stefan" "Zur Energetik"; "Ueber die Unentbehrlichkeit der Atomistik in der Naturwissenschaft"; "Ueber die Prinzipien der Mechanik": "Ueber eine These Schopenhauers."

Among the papers which do not deal with scientific subjects the "Reise eines deutschen Professors ins Eldorado" will probably arouse the most interest among American readers, since it describes the author's visit to this country in the summer of 1904, when he delivered a course of lectures at the University of California. While possessing a certain cynical humor this article seems out of place in a collection of scientific articles. The book would have gained in dignity by its omission.

E. M.

Die Moderne Theorie der physikalischen Erscheinungen. (Radioaktivität, Ionen, Elektronen.) By A. RIGHI. German translation by B. DERSAU. 8vo, pp. 152. Leipzig, Barth, 1905.

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La théorie moderne des phénomènes physiques: radioactivité, ions, électrons. By A. RIGHI. French translation by E. NÉCULCÉA. Preface by G. LIPPMANN. 8vo, pp. 126. Paris "L'Éclairage Électrique," 1906.

Trowbridge's English translation of Righi's interesting little book has already been referred to in these pages.[1] The appearance of the German and French translations gives evidence of the general favor with which the book has been received.

[1] PHYSICAL REVIEW, Vol. XXI., p. 205, September, 1905.

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THE

PHYSICAL REVIEW.

THE FREEZING OF PURE LIQUIDS AND SOLUTIONS UNDER VARIOUS KINDS OF POSITIVE AND NEGATIVE PRESSURE AND THE SIMILARITY BETWEEN OSMOTIC AND NEGATIVE PRESSURE.

By C. S. Hudson.

1. Introductory Note.

In a recent article concerning the relation between osmotic pressure and negative pressure Professor Geo. A. Hulett[1] has shown that the lower vapor-pressure of solutions indicates that the solutions are under a negative pressure, and a calculation of the negative pressure that would cause the observed depression shows that this negative pressure is exactly equal to the osmotic pressure of the solution. This important conclusion is to my knowledge the first evidence that osmotic pressure has the same effect on liquids as does negative pressure.

The question occurred to me on reading Professor Hulett's article whether the lower freezing-temperatures of solutions can also be the result of osmotic pressure acting as a negative pressure. At first sight this does not appear probable, because, since it is known that a positive pressure causes the freezing-temperature of water to sink, it would seem that a negative pressure would cause a rise of freezing temperature and that solutions should freeze above zero rather than below. This reasoning is not correct, however, because the ice which freezes from a solution is under atmospheric pressure,

[1] Zeitschrift für physikalische Chemie, *42*, 361, 1903.

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not negative pressure, and only the solution may properly be regarded as being under a negative pressure. The freezing-temperature of a liquid under such peculiar conditions of pressure is not known, and in order to calculate it I have investigated by thermodynamic methods the freezing of liquids under various kinds of pressure and this article presents the results of this inquiry. These results support without exception the view that osmotic pressure acts as a negative pressure.

2. INTRODUCTION.

In 1849 and 1850 James Thomson and Lord Kelvin showed by thermodynamic theory and by experiment that the freezing-temperature of water is lowered by a uniform pressure on the water and the ice to the extent of 0.00748° C. per atmosphere increase of pressure.

In 1881 J. H. Poynting[1] calculated from a thermodynamic cycle the change of freezing-temperature that is caused by an increase of pressure on the ice alone, such as might be realized for instance by the use of a rigid sieve in compressing the ice. Poynting showed that an increase of pressure of one atmosphere on the ice alone causes the freezing-temperature to sink 0.0899° C., a depression which is twelve times greater than that which is observed when the pressure is exerted uniformly on the water and the ice.

Recently it has been shown by G. N. Lewis[2] that if ice which is in equilibrium with water be subjected to a pressing[3] of dP, there will be no change of freezing-temperature provided the water is also subjected to the pressing dp that is fixed by the relation $dp/dP = V_i/V_w$, where V_i and V_w are the specific volumes of ice and water respectively. If these volumes are 1.0909 and 1.0001 cubic centimeters at 0°, $dp/dP = 1.09$; or, the increased pressing on the water must be nine per cent. greater than the increased pressing on the ice if the freezing-temperature is to remain unchanged. This relation can also be shown to result directly from a combination of

[1] Philosophical Magazine, (5), *12*, 32.

[2] Zeitschrift für physikalische Chemie, *38*, 207, 1901.

[3] I use the word *pressing* to signify a pressure that is exerted on one phase alone, in conformity with the use by Professor Ostwald of the German word *Pressung* to express the same idea.

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the calculations of Thomson and Poynting. First, let the water and the ice be subjected to the pressing dp, on account of which the freezing-temperature sinks (0.00748) dp degrees. Let the pressing on the ice be now diminished by d_1p, the pressing on the water being meanwhile kept constant, as a result of which the freezing-temperature rises (0.0899) d_1p degrees. If the rise of the freezing-temperature be made equal to its previous fall there is finally no change of freezing-temperature and therefore $(0.0899)d_1p = (0.00748)dp$. The total increase of pressing on the ice is $dp - d_1p = dP$, and the elimination of d_1p from the two equations gives $dp/dP = 1.09$, which is the relation that has been stated by Lewis.

Our present knowledge of the change of freezing-temperature with change of pressure can be condensed to Thomson's and Poynting's statements, which include, as I have just shown, Lewis' statement; and it is possible to calculate from the two coefficients 0.00748 and 0.0899 alone the freezing-temperature of water under all conditions of small pressure. To illustrate by an example the method of such a calculation let us find what is the freezing-temperature of water that is under the pressing of two atmospheres when its ice is under the pressing of six atmospheres. Ice and water are in equilibrium under a uniform pressure of two atmospheres at $-2(0.00748)$ degrees, and if the pressing of four atmospheres in addition be applied to the ice alone the freezing temperature will sink 4 (0.0899) degrees farther; and therefore the final freezing-temperature is 0.375° C. below zero.

On the other hand it is also possible in case the freezing-temperature and the pressing on either the solid or the liquid phase are known to calculate the unknown pressing on the other phase. Let us consider in this connection the following calculation concerning the freezing-temperatures of dilute aqueous solutions. The exact experiments of Raoult and others have agreed in showing that the molecular depression of the freezing-temperature of water is very nearly 1.84 degrees. As we know that the pure ice which freezes from such solutions is under atmospheric pressure we can calculate what mechanical pressing on pure water would cause it to freeze at -1.84 degrees, or in other words to behave exactly as the dilute solution does in so far as freezing is concerned. If the pressure p is applied

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uniformly to the ice and the water the freezing temperature sinks p (0.00748) degrees. If this pressure is removed from the ice but kept on the water the freezing-temperature rises p (0.0899) degrees. If the final depression of the freezing-temperature is 1.84 degrees we can write $p(0.00748) - p(0.0899) = 1.84$, and hence $p = -22.3$[1] atmospheres. For comparison with this value let us calculate the pressure that would be exerted by a perfect gas if its volume, temperature, and molal concentration were those of the solution. One mol of a perfect gas occupying the volume of one liter at zero degrees would exert the pressure of 22.4 atmospheres, and if its temperature were lowered 1.84 degrees its pressure would decrease to 22.3 atmospheres. The identity of this pressure which a perfect gas would exert if its volume, temperature, and molal concentration were those of the solution with the mechanical pressure that must be exerted on pure water to make it freeze at the same temperature as does the solution is a striking and instructive fact. It is evident from this simple calculation that the freezing-temperatures of solutions indicate that the solutions are under a negative pressure.

But before discussing this subject further I wish to examine the reasoning which has led to the accepted values of the coefficients of Thomson and Poynting in order to make certain that the use of them in studying the properties of solutions is valid. I shall now describe a thermodynamic cyclic process which shows the change of freezing-temperature that accompanies any change of pressure on the ice and the water. This cyclic process is not different in principle from those described by Thomson and Poynting, but it is of wider application.

3. Thermodynamic Investigation of the Process of Freezing.

Let the following cycle of operations be performed on a system which at the beginning is in the following condition: One gram of ice at the absolute temperature T is pressed upon with a pressing

[1] The physical interpretation of the negative sign of this pressure obviously is that the pressure is exerted in a direction tending to dilate the liquid. Such pressures as these, which are called negative pressures, have been realized and the behavior of water when subjected to them has been accurately determined by experiment. For a critical summary of our present knowledge of negative pressure in liquids the reader is referred to the previously mentioned article by Professor Hulett.

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of P by a piston which is permeable for water-vapor, but not for ice. Separate from this ice is a trace of water which is under the pressing p that is exerted by a piston that is permeable for water-vapor, but not for water. There is free communication for water-vapor throughout the system and its pressure is p'. It is obvious that the pressings P and p must be so selected that it is possible to have the common vapor pressure p' throughout. In such a system the total pressure on the ice is $P + p'$ and on the water $p + p'$.

Fig. 1.

Let the piston on the ice move down and the piston on the water move up until all the ice is evaporated at constant temperature and pressure. During this evaporation and condensation the piston on the ice moves through the volume V_i, the specific volume of ice, and the piston on the water moves through a volume that is slightly less than V_w, the specific volume of water, because the loss of volume resulting from the evaporation of the ice is slightly larger than the gain of volume resulting from the liquefaction of an equal mass of water-vapor. In order therefore to condense all the vapor that is formed from the ice it is necessary to move a piston that exerts the pressure p' on the vapor through the volume $V_i - V_w$. The total work that is obtained from the system during this first portion of the cycle is $pV_w - PV_i - p'(V_i - V_w)$, and the heat which must be supplied to the system in order to keep its temperature constant during the changes is L, the specific heat of fusion of ice.

Let the temperature of the system now sink dT degrees and let either p or P be reduced by an infinitesimal amount. The three pressures now are $p - dp$, $P - dP$, and $p - dp'$. The work that is done in changing these three pressures is so small on account of the very slight compressibility of water and ice that it may be neglected. At this lower temperature $T - dT$ let the pistons move in a manner reverse to that indicated before, thus doing the work $-(p - dp)V_w + (P - dP)V_i + (p' - dp')(V_i - V_w)$, while heat is abstracted from the system to keep its temperature constant. Let the temperature be now raised to its original value T and the pressures on the pistons be changed back to p, P, and p', respectively, the work done in changing then being again neglected.

The cyclic process is now complete, and since it is at every stage

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reversible, the second law of thermodynamics requires that the total gain in work divided by the fall in temperature equal the heat absorbed at the higher temperature divided by that temperature; or,

$$(dP/dT)V_i - (dp/dT)V_w + (dp'/dT)(V_i - V_w) = -L/T. \quad (1)$$

With the aid of this general relation let us now calculate the effect on the freezing-temperature of various typical changes of pressure.

4. Calculation of the Changes of Freezing Temperature that Accompany Typical Changes of Pressure.

Case 1. *The total change of pressure on the ice remains equal to the total change of pressure on the water.* In this case $dP + dp' = dp + dp'$, and the general equation (1) becomes $(dP + dp')/dT = -L/T(V_i - V_w)$. This is the well known relation that was shown by James Thomson. In the case of water and ice an increase of pressure of one atmosphere lowers the freezing-temperature 0.00748° C.[1]

Case 2. *The pressing on the water remains constant while the pressing on the ice is changed.* In this case $dp/dT = 0$ and therefore $dP/dT = -L/TV_i - (dp'/dT)(1 - V_w/V_i)$. Since one of the terms on the right of this equation is ten thousand times smaller than the other it can be neglected and the equation written $dP/dT = -L/TV_i$. This is the relation that was first shown by Poynting, and in the case of water it expresses the relation that an increase of pressing of one atmosphere on the ice alone lowers the freezing-temperature 0.0899° C.

Case 3. *The changes of pressing on the ice and the water are so related that the freezing-temperature remains constant.* In this case $dT = 0$, and therefore $(dp + dp')/(dP + dp') = V_i/V_w$. This is the equation that was derived by Lewis, which has been discussed in the introduction to this article.

Case 4. *The pressing on the ice remains constant while the pressing on the water is changed.* In this case $dP/dT = 0$, and therefore $dp/dT = L/TV_w + dp'/dT(V_i/V_w - 1)$; or, neglecting the small

[1] In this calculation and in the succeeding similar ones, the following data are used: latent heat of fusion of ice, 80.1 calories; mechanical equivalent of the calorie, 4.19(10)^7 ergs; atmospheric pressure, 1,013,200 dynes/cm.^{2}; specific volumes of ice and water at 0°, 1.0909 and 1.0001 cm.^{3} respectively.

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term as was done in case two, $dp/dT = L/TV_w$. This coefficient shows that if ice be kept under constant pressing while the pressing on the water is increased one atmosphere the freezing-temperature rises 0.0824°.

It seems to me that this fourth type of freezing, which to my knowledge has not been previously investigated, may occur in the natural freezings of winter weather whenever the conditions that are illustrated by the accompanying figure occur. The closed vessel A is supposed to contain air at atmospheric pressure and to be pierced by an open capillary tube whose lower end is immersed in water W. A piece of ice I is in the vessel and it is obvious that this ice is under the pressing of one atmosphere. Now it has been shown by Lord Kelvin[1] that the vapor-pressure of water which is in a capillary tube is less than that of a plane surface of water; from this fact we may conclude that the system shown in the figure will not be in equilibrium at zero degrees, but that at that temperature the ice will distil over to the water in the capillary tube. The temperature of equilibrium may be calculated as follows: The water in the capillary tube is under a pressing that is less than atmospheric by the hydrostatic pressure of the column of water. If the tube is so small that the capillary rise is (76 × 13.6) centimeters the pressing on the surface in the tube is decreased one atmosphere, and therefore according to the relation shown above the system will be in equilibrium at 0.0824° below zero. If the capillary rise is h centimeters the freezing-temperature is $(h \times 0.0824)/(76 \times 13.6)$ degrees below zero.

Fig. 2.

I wish now to show that this fourth case of freezing is also realized in the freezing of aqueous solutions. The reasoning by which this may be shown has already been given in an elementary form in the introduction to this article. It is obvious that in the freezing of solutions the ice is under atmospheric pressing and that the water is under atmospheric pressing altered by whatever pressing the dissolved substance may exert. If we assume that the dissolved substance exerts the same pressing as a perfect gas, the pressing p is

[1] Proceedings of the Royal Society of Edinburgh, 7, 63 (1870); Maxwell's Heat, 1877, 287.

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given by the relation $p = -cRT$, where R is the gas-constant and c is the concentration of the solution expressed in mols of dissolved substance per liter of solution. If this value of p is substituted in the coefficient of case four, we obtain $dT/dc = -(RT^2V_w)/L$. This expression is identical with the well known relation that Van't Hoff[1] first calculated from the osmotic theory of solution, and which has been repeatedly verified by exact experiments. From the agreement of these two expressions for the molecular depression of the freezing temperature with each other and with experiment we must therefore conclude that the freezing-temperatures of solutions indicate clearly that the solutions are under a negative pressure, comparable with a positive mechanical tension, and that this negative pressure or tension is caused by the dissolved substance and is identical with the osmotic pressure of the solution.

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[1] Lectures on Theoretical and Physical Chemistry. Volume 2.

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ON OPTICAL ROTATION.

By Herbert M. Reese.

THE writer was led some time ago to enquire what would be the diffraction-pattern produced by a rectangular opening through which passes a beam of light such that the amplitude is constant over the wave-front, but that the azimuth of the plane of polarization varies continuously and regularly from one side of the opening to the other. These conditions are approximately fulfilled when a beam originally plane-polarized is sent through a prism of some substance such as quartz, which rotates the plane of polarization. The elementary theory of diffraction was applied to this problem, and a result was obtained which seems to be of interest. Throughout the discussion no account was taken of the fact discovered by Fresnel, that in quartz a plane-polarized beam of light is broken up into two circularly-polarized beams, respectively right-handed and left-handed, with different velocities. But it was found in the end that this phenomenon was fully accounted for by the diffraction theory alone, with the simple assumption of rotation; thus showing that Fresnel's phenomenon may be regarded as the consequence of rotation instead of its cause.

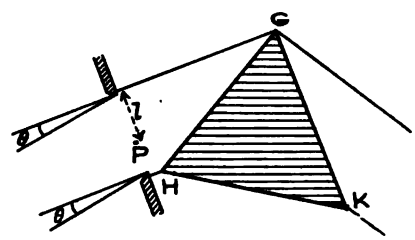

Fig. 1.

Suppose a quartz prism, *GHK* (Fig. 1), is traversed by a beam of light which emerges from the face, *GH*, so that the azimuth of the plane of vibration at any point, *P*, is proportional to the distance, *l*, from this point to the outer edge of the beam. That is, taking as zero the azimuth at the outer edge,

$$\text{azimuth} = nl.$$

Since transverse waves in mutually perpendicular planes cannot

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interfere, in order to determine the diffraction-pattern we must resolve the vibrations into components in two definite azimuths, and then treat each component separately. If we represent by $A \cdot dl$ the amplitude that would be produced in the focal plane by a strip of the wave-front of width dl, its components parallel to and perpendicular to the azimuth o are respectively $A \cos nl \cdot dl$ and $A \sin nl \cdot dl$. For the present we will concern ourselves only with the former.

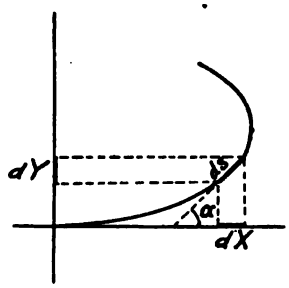

Fig. 2.

Let us find the amplitude of the disturbance produced in the focal plane at an angle θ with the axis of the beam. The phase-difference between the secondary waves coming from P and those coming from the edge of the beam is

$$\frac{2\pi}{\lambda} l \sin \theta = pl,$$

if we let $p = 2\pi/\lambda \sin \theta$. Therefore, if we apply the graphical vector method of Cornu[1] letting ds_x represent the amplitude of the disturbance from P, and α the angle ds_x makes with the X-axis on the vector diagram (*i. e.*, the phase) we have

$$ds_x = A \cos nl \cdot dl,$$

$$\alpha = pl.$$

Therefore:

$$dX_x = A \cos nl . \cos pl \cdot dl,$$

$$dY_x = A \cos nl \cdot \sin pl \cdot dl.$$

The subscript indicates that we are dealing only with vibrations parallel to the azimuth o. To integrate these expressions over the aperture and so find the resultant intensity due to all the vibrations in this direction, we can look upon the vector components X_x and Y_y as respectively the real and the imaginary part of the integral

$$S_x = \int_0^a A e^{ipl} \cos nl \cdot dl,$$

where a is the width of the beam. This gives

$$S_x = \frac{A}{n^2 - p^2}(n \sin na \cdot \cos pa - p \cos na \cdot \sin pa),$$

[1] Preston, The Theory of Light, 3d edition, arts. 45, 147.

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$$+\frac{Ai}{n^2-p^2}(n \sin na \sin pa + p \cos na \cos pa - p).$$

Therefore, we have

$$X_x = \frac{A}{n^2-p^2}(n \sin na \cos pa - p \cos na \sin pa),$$

$$Y_x = \frac{A}{n^2-p^2}(n \sin na \sin pa + p \cos na \cos pa - p),$$

and the resultant intensity is

$$I_x = X_x^2 + Y_x^2 = \frac{A^2}{(n^2-p^2)^2}\{n^2 \sin^2 na + p^2 \cos^2 na$$
$$+ p^2 - 2p(n \sin na \sin pa + p \cos na \cos pa)\},$$

while the phase of the resultant is given by

$$\tan \Phi_x = \frac{Y_x}{X_x} = \frac{n \sin na \cdot \sin pa + p \cos na \cos pa - p}{n \sin na \cos pa - p \cos na \sin pa}.$$

If we now consider those components of the vibrations which are perpendicular to the azimuth o we have

$$ds_y = A \sin nl \cdot dl,$$
$$dX_y = A \sin nl \cdot \cos pl\, dl,$$
$$dY_y = A \sin nl \cdot \sin pl\, dl.$$

These can be integrated by the same process used in the former instance, and we get

$$X_y = \frac{A}{n^2-p^2}(n - n \cos na \cos pa - p \sin na \sin pa),$$

$$Y_y = \frac{A}{n^2-p^2}(p \sin na \cos pa - n \cos na \sin pa),$$

$$I_y = \frac{A^2}{(n^2-p^2)^2}\{n^2 + n^2 \cos^2 na + p^2 \sin^2 na$$
$$- 2n(n \cos na \cos pa + p \sin na \sin pa)\},$$

$$\tan \Phi_y = \frac{p \sin na \cos pa - n \cos na \sin pa}{n - n \cos na \cos pa - p \sin na \sin pa}.$$

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Therefore the total intensity caused by the two components is

$$I = I_x + I_y = \frac{2A^2}{(n^2 - p^2)^2}\{n^2 + p^2 - 2pn \sin na \sin pa$$
$$- (n^2 + p^2)\cos na \cos pa\},$$

since I_x and I_y are in mutually perpendicular planes and therefore cannot interfere. Not only is this expression for the whole intensity of the illumination a function of p (and therefore of θ) but the phases Φ_x and Φ_y are also functions of θ, so that it is possible that the light transmitted in any direction θ may be either plane, elliptical or circular in polarization, depending upon the value of θ in terms of a and n. What we are most concerned with is the state of polarization at the maxima of intensity, so that our first step will be to find these maxima.

MAXIMA AND MINIMA.

A casual examination of the general formula, which can be put in the form

$$I = \frac{2A^2}{(n^2 - p^2)^2}\{(n^2 + p^2)(1 - \cos na \cos pa) - 2pn \sin na \sin pa\},$$

reveals the interesting fact that the center of the field is not necessarily a maximum. If we put $\theta = 0$ and, therefore, $p = 0$, we get

$$I = \frac{2A^2}{n^2}(1 - \cos na),$$

and if the width of the beam happens to be such that $\cos na = 1$ (a perfectly possible case) this reduces to 0. This shows that the center of the field may even be dark, and it will be shown later that it is in general either a minimum or a secondary maximum, unless the width of the beam is small.

The general condition for a maximum or a minimum is that $dI/dp = 0$,

$$\frac{dI}{dp} = \frac{2A^2}{(n^2 - p^2)^3}\{2p(3n^2 + p^2)(1 - \cos na \cos pa)$$
$$+ a(n^4 - p^4) \cos na \sin pa - 2n(3p^2 + n^2) \sin na \sin pa$$
$$- 2pna(n^2 - p^2) \sin na \cos pa\} = 2A^2 \frac{\varphi(p)}{(n^2 - p^2)^3}.$$

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The numerator $\varphi(p)$ vanishes for $p = 0$, $p = n$, and other values. The denominator also vanishes for $p = n$. To find the value of the fraction for this indeterminate case we must make successive differentiations. The first and second derivatives of the denominator vanish when $p = n$, the third reduces to $-48n^3$. The first and second derivatives of the numerator vanish when $p = n$, while the third reduces to

$$12 \sin^2 na - (12\, na + 8n^3a^3) \sin na \cos na.$$

Therefore $p = n$ gives a maximum or a minimum if $\sin na = 0$ or if

$$\tan na = \frac{na(3 + 2n^2a^2)}{3},$$

but not otherwise. Owing to the symmetry of the expression for I, if there is a maximum or a minimum when $p = p_1$, the same will occur when $p = -p_1$.

It will now be shown, however, that in any case if a is large there is a maximum or a minimum near $p = n$. Let us find the condition that a maximum or a minimum is given by $p = n + e$, where e is some small quantity. We can express $\varphi(n + e)$ in the following series form:

$$\varphi(n+e) = \varphi(n) + e\frac{d\varphi(n)}{dp} + \frac{e^2}{2}\frac{d^2\varphi(n)}{dp^2} + \frac{e^3}{3!}\frac{d^3\varphi(n)}{dp^3} + \frac{e^4}{4!}\frac{d^4\varphi(n)}{dp^4} + \cdots$$

$$= \frac{e^3}{3!}\frac{d^3\varphi(n)}{dp^3} + \frac{e^4}{4!}\frac{d^4\varphi(n)}{dp^4} + \cdots,$$

since, as we have just seen, $\varphi(n)$ and its first two derivatives vanish. Therefore we have

$$\frac{\varphi(n+e)}{[n^2 - (n-e)^2]^3} = \frac{-1}{e^3(2n+e)^3}\left\{\frac{e^3}{3!}\frac{d^3\varphi(n)}{dp^3} + \frac{e^4}{4!}\frac{d^4\varphi(n)}{dp^4} + \cdots\right\}.$$

The condition that the first two terms vanish is

$$e = -4\frac{d^3\varphi(n)}{dp^3} \div \frac{d^4\varphi(n)}{dp^4},$$

$$\frac{d^3\varphi(n)}{dp^3} = 12 \sin^2 na - (12na + 8n^3a^3) \sin na \cos na.$$

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$$\frac{d^4\varphi(n)}{dp^4} = 24a \cos na \sin na + 24na^2 (\sin^2 na - \cos^2 na) + 8n^3a^4.$$

Therefore, the condition is

$$\epsilon = \frac{-12 \sin^2 na + (12na + 8n^3a^3) \sin na \cos na}{32a \{3 \cos na \sin na + 3na (\sin^2 na - \cos^2 na) + n^3a^3\}}.$$

Therefore, if a is large, a small value of ϵ can be found which will make $\varphi(n+\epsilon)/(n^2-p^2)^3$ depend upon terms of the order $\epsilon^2/8n^3$, so that a maximum or a minimum occurs near $p = \pm n$.

Fig. 3 is drawn to scale so as to show the relation between I and

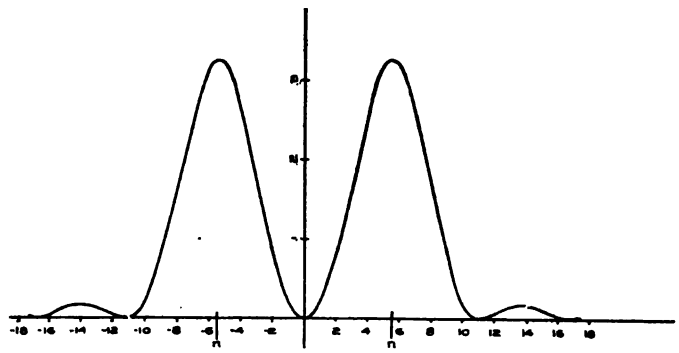

Fig. 3.

p where n has the value 5.52 (about the value for an actual quartz prism belonging to the University of Missouri) and $na = 2\pi$. Fig. 4 shows the same thing where $na = 7\pi/2$. Curves have been plotted for a number of other cases; and in every case except for unusually small values of na (less than π) the intensity at the middle of the field is zero or very small, a large maximum occurs where $p = \pm n$ or near there, and there are several small maxima. Hence the general effect is to produce a double line in the focal plane. The polarization of this doublet will be considered later.

Hereafter we will confine our attention to the case where $\sin na = 0$ and $\cos na = 1$. In this case the general formula for I becomes much simpler and can be handled more easily. Moreover we have seen that under such circumstances a maximum or a minimum is given by $p = n$; and we know from physical considerations that

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any such conclusions drawn for this case will apply approximately to any other, provided na be large. For, suppose $na = 2\pi k$, where k is a large integer, then the additional width of beam necessary to make $na = 2\pi(k + e)$, where e is any number between 0 and 1, will

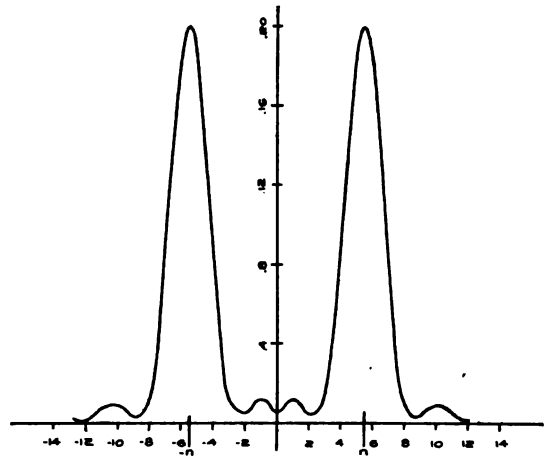

Fig. 4.

be small compared to the original width, and therefore will not seriously affect the diffraction pattern.

If we put $\sin na = 0$ and $\cos na = 1$, the general formula becomes

$$I = \frac{2A^2}{(n^2 - p^2)^2}(n^2 + p^2)(1 - \cos pa),$$

and the condition for a maximum or a minimum is

$$\frac{1}{(n^2 - p^2)^3}\{2p(3n^2 + p^2)(1 - \cos pa) + (an^4 - ap^4)\sin pa\} = 0.$$

We have seen that this vanishes when $p = n$. To determine whether it is a maximum or a minimum, we take the second derivative:

$$\frac{1}{2A^2}\frac{d^2I}{dp^2} = \frac{1}{(n^2 - p^2)^4}\{(6n^4 + 36n^2p^2 + 6p^4)(1 - \cos pa)$$
$$+ (12apn^4 - 8ap^3n^2 - 4ap^5)\sin pa$$
$$+ (a^2n^6 - a^2n^4p^2 - a^2n^2p^4 + a^2p^6)\cos pa\} = \frac{M}{Q}.$$

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Both M and Q and their first three derivatives vanish when $p = n$; but

$$\frac{d^4 M}{dp^4} = -16n^2a^2(n^2a^2 - 1),$$

$$\frac{d^4 Q}{pd^4} = 384n^4$$

Therefore

$$\frac{1}{2A^2}\frac{d^2 I}{dp^2} = -\frac{16n^2a^2(n^2a^2 - 1)}{384n^4} = -\frac{a^2}{24n^2}(a^2n^2 - 1).$$

Since $na = 2\pi k$, where k is a positive integer, d^2I/dp^2 is negative. Therefore I is a maximum. Hence, since the two principal maxima occur at $p_1 = n$ and $p_2 = -n$, their angular separation is given by

$$p_1 - p_2 = \frac{2\pi}{\lambda}\sin\theta_1 - \frac{2\pi}{\lambda}\sin\theta_2 = 2n,$$

or, approximately,

$$\theta_1 - \theta_2 = \frac{n\lambda}{\pi}.$$

POLARIZATION AT THE PRINCIPAL MAXIMA.

If, in the expressions for Φ_x and Φ_y, we put $\sin na = 0$ and $\cos na = 1$ we get for the phases of the two mutually perpendicular components of the vibrations

$$\tan\Phi_x = \frac{1 - \cos pa}{\sin pa},$$

$$\tan\Phi_y = \frac{-\sin pa}{1 - \cos pa}.$$

From the form of these expressions it is evident that Φ_x, Φ_y, and therefore $\Phi_x - \Phi_y$ have opposite signs on the two sides of the center of the field (*i. e.*, changing the sign of p changes the sign of each). If we put $p = n$, remembering that $\sin na = 0$, $\cos na = 1$, these take indeterminate forms which reduce to

$$\tan\Phi_x = 0 \qquad \text{or} \qquad \Phi_x = 0 \text{ or } \pi,$$

$$\tan\Phi_y = -\infty \qquad \text{or} \qquad \Phi_y = \pm\frac{\pi}{2}.$$

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If we put $p = -n$,

$$\tan \Phi_x = 0 \qquad \text{or} \qquad \Phi_x = 0 \text{ or } \pi,$$

$$\tan \Phi_y = -\infty \qquad \text{or} \qquad \Phi_y = \pm \frac{\pi}{2}.$$

Therefore, since for the two values $p = n$ and $p = -n$ the phase-difference is equal to $\pi/2$ in each case but of opposite signs, the angles corresponding to these values will give directions along which the transmitted light is circularly polarized in opposite senses, provided only that I_x and I_y are equal in each case. This is easily seen to be true from the original formulæ, for

$$I_x = \frac{2A^2}{(n^2 - p^2)^2}(p^2 - p^2 \cos pa),$$

$$I_y = \frac{2A^2}{(n^2 - p^2)^2}(n^2 - n^2 \cos pa).$$

And these become identical when $p = \pm n$, and although each becomes indeterminate in form, each reduces to the value $A^2a^2/2$.

We have thus arrived at an explanation of the phenomenon observed by Fresnel without making any assumption as to the velocity of circularly polarized light in the prism. However, it will be shown later that the mere fact of rotation is a proof that the apparent velocities of right-handed and of left-handed circularly-polarized light are different in the rotating medium; and therefore the explanation by Fresnel and that given here are equivalent.

In order to see whether the angular separation predicted by the above theory is the same as that required in Fresnel's theory, it is necessary to express the latter in terms of the quantity n.

In Fig. 5,

$$l = s \sin B,$$

$$d = 2s \sin \tfrac{1}{2}A.$$

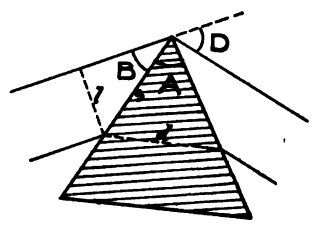

Fig. 5.

If v and $v + dv$ represent the velocities of the two rays in quartz and λ' the wave-length in quartz, then the phase-difference between the two rays on emerging is

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$2\pi/\lambda' v\, dv$. Therefore, the rotation, which is half the phase-difference is

$$\varphi = \frac{\pi d}{\lambda' v} dv.$$

We have defined n as φ/l, therefore,

$$n = \frac{\pi d}{\lambda' v l} dv = \frac{2\pi}{\lambda'} \frac{dv}{v} \frac{\sin \frac{1}{2}A}{\sin B}.$$

But $A + 2B = 180° - D$, therefore,

$$n = \frac{2\pi}{\lambda'} \frac{dv}{v} \cdot \frac{\sin \frac{1}{2}A}{\cos \frac{1}{2}(A + D)}.$$

From the formula for the refractive index, we have

$$\frac{v_0}{v} = \frac{\sin \frac{1}{2}(A + D)}{\sin \frac{1}{2}A},$$

where v_0 is the velocity in air. Therefore,

$$\frac{dv}{v} = -\frac{v}{2v_0} \frac{\cos \frac{1}{2}(A + D)}{\sin \frac{1}{2}A} \cdot dD.$$

Substituting this we get

$$n = -\frac{\pi}{\lambda'} \frac{v}{v_0} dD.$$

Since $\lambda' v_0/v = \lambda$, the wave-length in air, we have

$$n = -\frac{\pi}{\lambda} \cdot dD,$$

$$dD = \theta_1 - \theta_2 = -\frac{\lambda n}{\pi}.$$

This is the same angular separation as that given above by the diffraction theory, the difference in sign being of no consequence.

CIRCULARLY-POLARIZED LIGHT.

Suppose the light entering the prism, instead of being plane, were circularly-polarized, say in the right-handed sense. To find the form of the diffraction pattern we must suppose the vibrations broken up into two mutually perpendicular ones with a phase-dif-

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ference of $\pi/2$, and treat each separately. We will as before confine our attention to the special case where $\sin na = 0$ and $\cos na = 1$. Each of the parts into which we have divided the incident light will produce in the focal plane two mutually perpendicular components of the types I_x and I_y. The I_x due to the second part of the incident beam will be parallel to the I_y of the first part and in the same direction, while the I_y of the second part will be parallel to the I_x of the first part but in the *opposite* direction. Let I_x', I_y', X_x', Y_x', X_y', Y_y', etc., refer to the first part of the incident beam, I_x'', I_y'', X_x'', etc., to the second part. Then we have, since I_y'' is opposite in direction to I_x',

$$X_x' = -\frac{Ap}{n^2 - p^2}\sin pa, \qquad X_y' = \frac{An}{n^2 - p^2}(1 - \cos pa),$$

$$Y_x' = -\frac{Ap}{n^2 - p^2}(1 - \cos pa), \qquad Y_y' = \frac{-An}{n^2 - p^2}\sin pa,$$

$$X_x'' = \frac{-Ap}{n^2 - p^2}\sin pa, \qquad X_y'' = \frac{-An}{n^2 - p^2}(1 - \cos pa),$$

$$Y_x'' = -\frac{Ap}{n^2 - p^2}(1 - \cos pa), \qquad Y_y'' = \frac{An}{n^2 - p^2}\sin pa.$$

Since there is a phase-difference of $\pi/2$ between I_x' and I_y'', I_y' and I_y'', we have for the resultant components on the vector diagram,

$$X_x = X_x' - Y_y'' = \frac{A \sin pa}{p - n},$$

$$Y_x = Y_x' + X_y'' = \frac{A(1 - \cos pa)}{p - n},$$

$$X_y = X'_y - Y_x'' = -\frac{A(1 - \cos pa)}{p - n},$$

$$Y_y = Y_y' + X_y'' = \frac{A \sin pa}{p - n}.$$

Let us substitute in these formulæ the value $p = n$. All become indeterminate in form but reduce to the following :

$$X_x = \frac{Aa \cos pa}{1} = Aa,$$

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$$Y_x = \frac{Aa \sin pa}{1} = 0,$$

$$X_y = -\frac{Aa \sin pa}{1} = 0,$$

$$Y_y = \frac{Aa \cos pa}{1} = Aa.$$

This indicates a simple circularly-polarized beam. On the other hand, if we put $p = -n$ we get

$$X_x = Y_x = X_y = Y_y = 0.$$

Therefore, if circularly-polarized light passes into the prism, one member of the usual doublet in the focal plane is missing, and the other is circularly polarized, like the incident light. Hence we may say that circularly-polarized light passes through the prism unaltered, the deviation being different for right-handed and for left-handed beams.

It is not to be understood that this theory is offered as a substitute for that of Fresnel, or that the claim is made that it is simpler or preferable in any way. Its aim is to show that instead of regarding the rotation of the plane of polarization as a consequence of the fact that right-handed and left-handed beams travel with different velocities, we may just as truly regard the latter fact as a consequence of the former. Fresnel's so-called explanation of rotation is not really a relation between cause and effect, but merely a mathematical point of view, and the point of view presented in this paper is just as good.

It has been shown by H. T. Eddy[1] that a difference between the velocities follows as a consequence of the rotatory power of the medium, by methods entirely different from those used here. It is not necessary, however, to use analytic methods to prove this, as the following purely geometrical considerations will show. Suppose

[1] PHYS. REV., XX., April, 1905.

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we have a parallel-sided plate of a material with right-handed rotatory power, and incident upon it a right-handed circularly-polarized beam. Suppose the beam to be analyzed into two plane-polarized beams in planes at right-angles, with a phase-difference of $\pi/2$. Each of these in passing through the plate will have its plane rotated by a certain amount. Suppose the thickness of the plate to be such that it contains n wave-lengths of the plane-polarized beams. On emerging from the plate the two beams can be regarded as again producing circularly-polarized light, but owing to the rotation which each has experienced the new beam will have suffered an advance in phase which is equivalent to a shortening of the wave-length, as if there were now more than n waves in the thickness of the plate. This again is equivalent to a decrease in velocity. On the other hand, if the incident light had been left-handed, there would have been an apparent increase in wave-length and in velocity. Hence, if the velocity be measured by any interferential method, or by any other means depending upon the wave-length, we will obtain a different velocity for the two kinds of light. However, there is no reason at all to suppose that, if the velocity were measured by the fundamental method of the rotating mirror or the toothed wheel, any difference would be observed; on the other hand it is hard to conceive how, measured in this way, the velocity of a circularly polarized ray should be any different from that of the plane-polarized rays to which it is equivalent. We may say that there is a difference in the wave velocity, but not in the group velocity. It seems to the writer that this distinction is rather important. One can form a mental picture of this condition by imagining a long rotating corkscrew. The apparent wave-motion has a certain velocity, but a point moving along the screw and following its convolutions (which point can represent the van of a train of waves) might have a velocity in the direction of the waves greater or less than this.

Of course it is needless to point out that whatever results have been arrived at in this paper apply equally well to any other optically rotating medium as well as quartz, whether this rotating power be a natural quality of the material or be induced by magnetic effects.

A summary of the points brought out is here presented:

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1. The separation of a plane-polarized beam into two circularly-polarized beams with different deviation is explained by the theory of diffraction alone.

2. The difference in the apparent velocity of right-handed and left-handed circularly-polarized waves is also accounted for by the same theory.

3. This difference only applies to the velocities as measured by interference methods. The group velocity, or the velocity of the front of a train of waves, is independent of the polarization.

4. This theory is mathematically equivalent to that of Fresnel, the two being merely the result of different points of view.

UNIVERSITY OF MISSOURI,
January 2, 1906.

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STUDIES IN LUMINESCENCE.

VI. The Decay of Phosphorescence in Sidot Blende.[1]

By Edw. L. Nichols and Ernest Merritt.

THE decay of phosphorescence was first studied by E. Becquerel.[2] In the case of short-duration phosphorescence the phosphoroscope was used for this purpose and the intensity of phosphorescence was measured for different speeds of the rotating disc. Becquerel regarded it as probable that the law of decay was of the form

$$I = I_0 \epsilon^{-at}, \tag{1}$$

and found that the observations were in fact fairly well represented by an exponential expression. In discussing these observations, however, Becquerel tacitly assumed that no appreciable time was required for the exciting rays to produce their full effect. Later investigations have shown that this assumption is not justified. Since a change in the speed of the phosphoroscope altered not only the time that elapsed between excitation and observation, but also the duration of exposure, it is probable, therefore, that the initial excitation was less at high speeds. Attention was directed to this point by E. Wiedemann and later by H. Becquerel, who states that a recomputation of the data shows a less satisfactory agreement with the exponental law than at first appeared.

For the long-time phosphorescence of the phosphorescent sulphides E. Becquerel proposed an empirical expression of the form

$$I^m(c + t) = cI_0^m. \tag{2}$$

For each of the seven substances tested this expression was found to show a fairly good agreement with the experimental results

[1] An account of the work described in this paper was presented to the American Physical Society at the meeting held on Oct. 28, 1905. An abstract appeared in the Physical Review, Vol. XXI., p. 411, December, 1905.

[2] Becquerel, "La Lumière." See also Comptes Rendus, Vol. 51, p. 921, 1860, and Annales de Chimie et de Physique, Series 4, Vol. 62, p. 5.

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throughout a considerable range. In one case, namely that of a calcium sulphide preparation giving an orange-red phosphorescence, the expression represented the observations with considerable accuracy throughout the whole range, the value of m being 0.5. But in most cases it was not possible to find values of m and c which would make the formula fit the experimental data for the whole time of decay. The values of m that suited the observations best lay between 0.5, for the calcium sulphide just mentioned, and 0.806 for another calcium sulphide having an orange yellow phosphorescence.

The same empirical formula has since been very generally used; among others by Darwin[1] in 1881, and Ch. Henry[2] in 1892. The former worked with Balmain's paint and found the best value for m to be 0.86. It cannot be said, however, that the experimental results were represented very accurately by the formula. The substance used by Henry was Sidot's blende, several different samples of which were tested. Henry states that in the case of one specimen the results were represented by an exponential law (eq. 1) for 14 seconds, while other preparations obeyed the law

$$t^{0.5936}(t + 27.18) = 1{,}647.5 \qquad (3)$$

Henry appears to have been convinced of the corrections of the latter law and proposed a new type of photometer which made use of the gradually decaying phosphorescence of Sidot blende in the measurement of faint sources of light.[3] While the fact that the constant in eq. (3) is given to five significant figures indicates an accuracy that is unusual in photometric measurements, the lack of experimental data in the paper referred to makes it difficult to form an independent opinion of the significance of the conclusions.

The decay of phosphorescence was considered from the theoretical standpoint by H. Becquerel[4] in 1891. Upon the assumption that the light emitted during phosphorescence was due to molecular vibrations set up by the action of the exciting light and afterwards gradually dying out, it was shown that the law of decay would be

[1] Philosophical Magazine, Vol. 11, p. 209, 1881.
[2] Comptes Rendus, Vol. 115, p. 505, 1892.
[3] Comptes Rendus, Vol. 115, p. 602.
[4] Comptes Rendus, Vol. 113, p. 618, 1891.

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determined by the nature of the damping forces. If the vibrations meet with an opposing force proportioned to the speed it was shown that an exponential law of decadence would result; while if the resistance is proportional to the square of the speed the law of decadence would take the form

$$I = \frac{1}{(a + bt)^2}. \tag{4}$$

It will be noticed that the emprical law proposed by E. Becquerel reduces to (4) in case $m = 0.5$.

In the case of a substance whose phosphorescent spectrum contains several bands Becquerel proposed the expression

$$I = \Sigma \frac{1}{(a + bt)^2}, \tag{5}$$

in which there is one term in the summation for each band. Upon testing this law with the data obtained by E. Becquerel for a calcium sulphide giving blue phosphorescence it was found that the results could be expressed by the use of two terms in the above series with great accuracy. The existence in the spectrum of this substance of two bands possessing independent properties could be demonstrated in various ways.

In the derivation of the law proposed by H. Becquerel the assumption is that the vibrations set up by the action of the exciting light continue during several minutes or even hours. This would imply either that the vibrating atoms or molecules exist during this time without collisions with other molecules, or else that such collisions are without effect upon the vibrations. Neither of these suppositions seems to us tenable. But the law nevertheless appears to be of very general application. We shall show later that the same law may be derived from entirely different theoretical considerations.

In all of the experiments upon the decay of phosphorescence with which we are familiar it is the total light that has been measured; so far as we are aware no attempt has been made to determine the law of decay for different portions of the phosphorescence spectrum. This fact complicates the problem greatly, for in most

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cases of phosphorescence the spectrum consists of two or more bands, which, in general, decay at different rates. It can hardly be expected, therefore, that measurements of the total light will be found to obey a simple law. The difficulties resulting from the complexity of the luminescence spectrum were recognized by E. Becquerel and were several times mentioned in the course of his classic researches. In discussing his experiments on decadence he suggested an expression of the form

$$I = Ae^{-\alpha t} + Be^{-\beta t} + \cdots \tag{6}$$

for the intensity of the total phosphorescence, with one term for each band in the spectrum. But the difficulties of computation were such as to lead him to abandon this expression and to employ instead the empirical expression of eq. (2). Recognition of the fact that each band has its own rate of decay is also implied in the law proposed by H. Becquerel (eq. 4).

EXPERIMENTAL.

While it is possible to test the corrections an expression of the form of (4) or (6) by comparison with measurements of total intensity, such a test is difficult, and cannot be altogether satisfactory; for with an expression containing several terms the number of constants is so great that the law may be made to fit almost any data. It is clear that a much more severe test of any given law of decay may be obtained from experiments with a substance having only one band in its phosphorescence spectrum. The Sidot blende screen used by us in earlier experiments[1] was found to have three bands in its luminescence spectrum. But since the two violet bands do not appreciably overlap the green band the spectrophotometer enables the behavior of the latter band alone to be conveniently studied. The matter is still further simplified by using the violet rays of the arc in excitation, since these rays, while they produce a brilliant green luminescence, are incapable of exciting either one of the violet bands.[1] In view of the brilliancy of the green band, its long duration, and the ease in which it may be isolated, this band seems well adapted to the study of the decay of phosphorescence.

Our previous experiments on Sidot blende have shown that in the case of the green band the phosphorescence spectrum shows no

[1] PHYSICAL REVIEW, Vol. XXI., p. 247, 1905.

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measurable change in form during the first ten seconds of decay. In other words, the rate of decay is the same for all wave-lengths. To fix the behavior of the whole band it would be sufficient, therefore, to determine the law for a single wave-length. We have, however, made measurements at three different wave lengths, namely, at 0.483 μ, 0.512 μ and 0.547 μ. The first of these wave-lengths lies near the ultra edge of the band; the second is not far from the maximum; and the third is near the red edge.

The methods of measurement were the same as those described in our last paper.[1] The experimental data obtained are contained

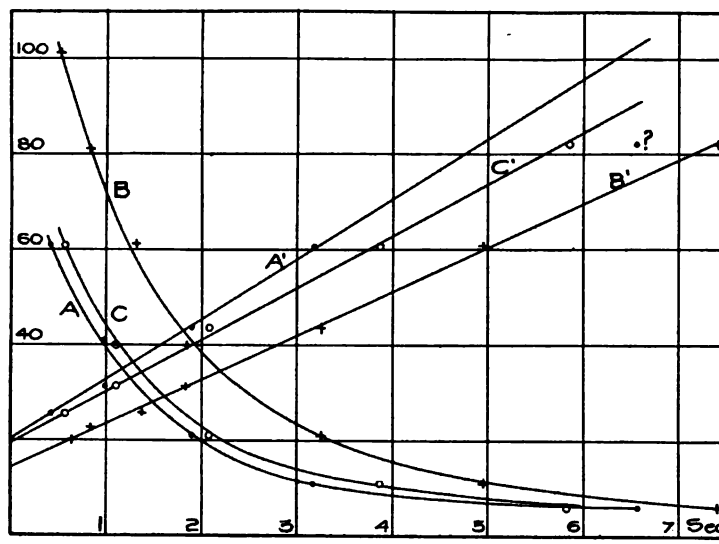

Fig. 36. Curves A, B and C show the decay in the phosphorescence of Sidot blende for the wave-length 0.483 μ, 0.512 μ and 0.547 μ, respectively. The curves A', B' and C' are obtained from A, B and C by plotting $I^{-\frac{1}{2}}$ instead of the intensity of phosphorescence, I.

in the following three tables. In each case it is the average of from ten to twenty observations that is recorded.

In the set of observations contained in Table I. the curves for 0.547 μ, 0.483 μ and 0.512 μ were determined during the forenoon in the order just stated. The data for 0.512 μ with weaker excitation were observed during the afternoon of the same day.

[1] PHYSICAL REVIEW, Vol. XXI., p. 247, 1905.

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The observations recorded in Table II. were taken in a different manner, the measurements at a given intensity being made for each of the three wave-lengths in succession. The observations of December 13 (Table III.) were made in a similar manner. The first three curves of Table I. are plotted in Fig. 36, while the second and fourth curves of this table are shown in Fig. 37.

TABLE I. [NOV. 25.]

Time in Seconds Required for the Phosphorescence to Fall from its Initial Intensity to the Intensity I. The Computed Values of t are Derived by Substitution in the Following Equations:

For $\lambda = 0.483\,\mu$ $\quad 1/\sqrt{I} = 0.102 + 0.059\,t$

$\lambda = 0.512\,\mu$ $\quad 1/\sqrt{I} = 0.074 + 0.045\,t$

$\lambda = 0.547\,\mu$ $\quad 1/\sqrt{I} = 0.096 + 0.055\,t$

$\lambda = 0.512\,\mu$ (weaker excitation) $\quad 1/\sqrt{I} = 0.092 + 0.052\,t$

I	λ = 0.483 μ		λ = 0.512 μ		λ = 0.547 μ		λ = 0.512 μ Weaker Excitation.	
	t sec. Obs.	t sec. Comp.	t sec. Obs.	t sec. Comp.	t sec. Obs.	t sec. Comp.	t sec. Obs.	t sec. Comp.
101			0.63	0.58				
81			0.83	0.85				
61	0.41	0.44	1.38	1.20	0.56	0.58	0.72	0.69
41	0.99	0.92	1.84	1.83	1.10	1.09	1.24	1.23
21	1.88	1.98	3.25	3.23	2.07	2.23	2.42	2.45
11	3.16	3.39	4.95	5.10	3.87	3.74	4.03	4.04
6	6.55	5.23	7.42	7.50	5.82	5.71	6.22	6.92

TABLE II. [DEC. 10.]

Time in Seconds Required for the Phosphorescence to Fall to the Intensity I. The Computed Values of t are Derived by Substitution in the Following Equations:

For $\lambda = 0.512\,\mu$ $\quad 1/\sqrt{I} = 0.078 + 0.034\,t$ $\quad \lambda = 0.547\,\mu$ $\quad 1/\sqrt{I} = 0.104 + 0.042\,t$

I	λ = 0.483 μ		λ = 0.512 μ		λ = 0.547 μ	
	t sec. Observed.	t sec. Computed.	t sec. Observed.	t sec. Computed.	t sec. Observed.	t sec. Computed.
81.4	0.60		1.06	0.98	0.30	0.22
61.4	0.77		1.35	1.49	0.55	0.62
31.4	2.40		2.98	3.02	1.83	1.84
11.4	4.13		6.47	6.46	4.62	4.58

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TABLE III. [DEC. 13.]

Time in Seconds Required for the Phosphorescence to Fall to the Intensity I. The Computed Values of t are Derived by Substitution in the Following Equations:

For $\lambda = 0.483\ \mu$ $1/\sqrt{I} = 0.104 + 0.070\,t$ $\lambda = 0.547\ \mu$ $1/\sqrt{I} = 0.118 + 0.070\,t$
$\lambda = 0.512\ \mu$ $1/\sqrt{I} = 0.094 + 0.046\,t$

I	$\lambda = 0.483\ \mu$		$\lambda = 0.512\ \mu$		$\lambda = 0.547\ \mu$	
	t sec. Observed.	t sec. Computed.	t sec. Observed.	t sec. Computed.	t sec. Observed.	t sec. Computed.
81.4			0.45	0.37		
61.4	0.45	0.36	0.69	0.74	0.25	0.14
31.4	1.06	1.08			0.88	0.87
21.4	1.46	1.61	2.60	2.67	1.30	1.40
11.4	2.78	2.76	4.48	4.44	2.61	2.55
7.4	4.46	3.80	5.97	6.00	4.58	3.57

The data of the preceding tables have been used to test the applicability of each of the several proposed laws of decay to the case of a single band. It was found that the results can be closely represented by an expression of the form given in eq. (4). To determine the constants a and b of this equation a convenient graphical method was employed, in which the values of $1/\sqrt{I}$ were plotted as ordinates and times as abscissas. Since eq. (4) may be written in the form

$$\frac{1}{\sqrt{I}} = a + bt,$$

the points located in this manner should lie on a straight line. A straight line having been drawn as nearly as possible through all the points, the slant of this line and its y intercept at once gave the values of b and a respectively. The values of a and b determined in this way are given in each of the tables, and the values of t computed from the above equation are tabulated for comparison with the times observed.

In Figs. 36 and 37 the values of $I^{-1/2}$ have been plotted as described above. It will be noticed that in each case the points lie very nearly upon a straight line, and that there is nothing to indicate any systematic variation from linearity. In the case of one curve, namely that for 0.483 μ in Table II., the points located in this

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way did not lie even approximately on a straight line. This curve, therefore, does not have the form corresponding to eq. (4). But in the case of the other curves, including one taken at this same wave-length (Table I.), the agreement between the observed and computed values of t is satisfactory, the differences being only such as might well result from accidental errors. It seems probable therefore that the observations at 0.483 μ in Table II. were subject to some unusual source of error.

In Fig. 36 it will be noticed that one point of the line A' (indi-

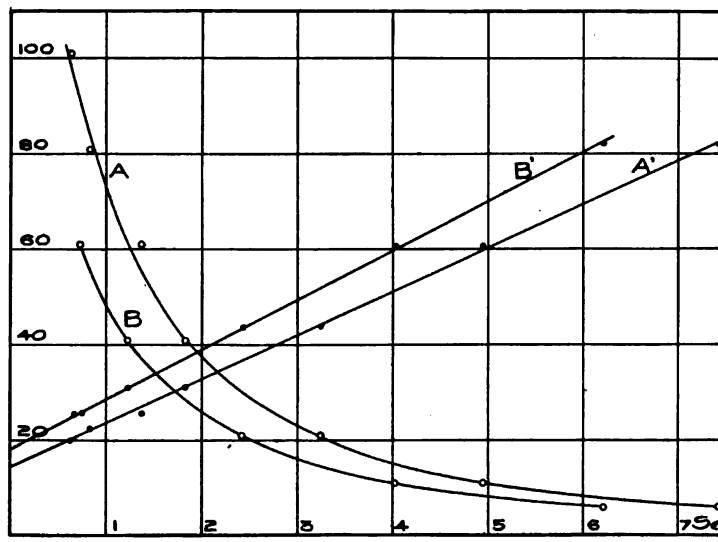

Fig. 37. Curves A and B show the decay of phosphorescence at 0.512 μ for two different intensities of the exciting light. In the curves A' and B' $I^{-\frac{1}{2}}$ is plotted instead of the intensity I.

cated by a question mark) falls below the line, *i. e.*, the observed time of decay was considerably greater than that computed from an assumed linear relation between $I^{-\frac{1}{2}}$ and t. Discrepancies of the same kind will be found for the smallest values of I in the first curve of Table I. and for the first and last curves of Table III. No such discrepancies are present in any of the four curves taken at 0.512 μ—*i. e.*, near the maximum of the phosphorescence spectrum. If these cases of disagreement between the observed and computed values of t are not due to accidental errors,

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they show that the violet edge of the phosphorescence band dies out more gradually than the maximum. Our previous observations[1] had indicated that if any difference exists between the two rates, the violet end of the band decays more rapidly than the center. Because of these conflicting indications, and especially because of the difficulties of making accurate readings for small intensities, we are inclined to ascribe the seeming variations from linearity to accidental errors.

THEORETICAL.

In attempting to interpret the results of the foregoing experiments we have found it useful to consider the subject from the standpoint of a hypothesis first proposed in explanation of luminescence phenomena by E. Wiedemann[2] and later modified and extended by Wiedemann and Schmidt.[3] According to this view some chemical or physical change is produced in a luminescent substance during excitation, and the emission of light is an accompaniment of the more or less gradual restoration of the modified substance to its original condition. Thus, in the case of phosphorescence, it was suggested by Wiedemann that a portion of the active material was changed by the exciting light from the stable condition *A* into the unstable state *B*. Phosphorescence would then result from a gradual breaking down of the unstable compound.[4] Wiedemann pointed out that this hypothesis leads to an exponential law of decay.[5]

While the change called for by the theory here considered has usually been assumed to be of a chemical nature, it was pointed out

[1] PHYSICAL REVIEW, Vol. XXI., p. 257.

[2] E. Wiedemann, Zur Mechanik des Leuchtens. Wied. Ann., Vol. 37, p. 177, 1889.

[3] E. Wiedemann und G. C. Schmidt. Wied. Ann., Vol. 56, p. 177, 1895.

[4] "Das auffallende Licht ruft chemische Modificationen in den phosphorescierenden Körpern hervor, die nachher wieder im umgekehrten Sinne durchlaufen werden und dabei eine Lichtentwickelung hervor rufen. . . . In Bezug auf die chemische Veränderungen dürfte die Anschauung wahrscheinlich sein, dass das Schwefelcalcium etc. in zwei Modificationen, einer stabilen und einer labilen *A* und *B*, bestehen kann. Die Modification *A* wird durch Absorption gewisser Strahlen in die Modification *B* verwandelt, welche allmählich unter Lichtentwickelung sich in *A* zurück verwandelt. . . . Da die Substanzen schon während der Belichtung phosphorescieren, so muss die Rückbildung auch während derselben vor sich gehen." E. Wiedemann, l. c., p. 224–5.

[5] Wiedemann, l. c., p. 226.

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by Wiedemann and Schmidt[1] that in many cases there were reasons for looking upon electrolytic dissociation as the more probable cause of luminescence. The increased conductivity of fluorescent solutions during fluorescence[2] adds support to this view. But although it is probable that the exciting light causes a separation of the active molecule into positive and negative parts, it appears to us unlikely that these parts are the ions of ordinary electrolysis. There are many substances like fluorescein and eosin which fluoresce only when dissociated. In such cases fluorescence cannot be due to the recombination of ions; for dissociation and recombination are taking place in an electrolytic solution all the time, and if this were the cause of luminescence we should expect the solution to glow continuously without the action of any exciting light. Fluorescence in such cases must be due to some action of the exciting light upon one of the ions. We have suggested elsewhere that this action may be a dissociation similar to that produced in gases by the Roentgen rays.

Assuming the correctness of the Wiedemann hypothesis in its general features it seems clear that dissociation in the case of photo-luminescence is a result of the violent vibrations set up in the molecules of the active substance by the exciting light. A certain number of the active molecules are actually torn apart, and the resulting negative electrons and positive nuclei exist for a time uninfluenced by their mutual attraction. The vibrations that occur upon the recombination of the ions give rise to luminescence. This view at once explains the well known fact that the light from an isotropic luminescent body is unpolarized, whatever may be the state of polarization of the exciting light.[3]

The fact that the light emitted during luminescence is of different wave-length from the exciting light seems at first to speak against the above explanation of photo-luminescence. Why should the vibrations that occur on recombination differ in period from those originally set up by the exciting light? It is indeed possible that the latter are forced vibrations, whose period bears no simple rela-

[1] L. c., pp. 244–247.

[2] Nichols & Merritt, PHYSICAL REVIEW, Vol. 19, p. 396, 1904.

[3] Seeming exceptions to this statement probably result from polarization by emission. See Millikan, PHYSICAL REVIEW, Vol. 3, p. 97.

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tion to the natural period of the molecule. But it is more reasonable to expect that vibrations which bring about actual disintegration are produced by resonance. If this is true we have to do with the natural period of the molecule in both cases, and it would seem that the light emitted during luminescence should have the same wave-length as the exciting light. In the discussion that follows we venture to make a suggestion which offers an explanation of this difficulty.

In the case of photo-luminescence in solids and liquids the active molecule is always closely surrounded by other molecules. In general these surrounding molecules belong to the solid or liquid solvent in which the active material is dissolved. If we have to deal with the luminescence of a pure substance (if such cases occur), the surrounding molecules are of the same kind as those which participate in the luminescence phenomena. But in either case the period of vibration will be different from what it would be if the vibrating molecules were isolated. Since the change in period will be relatively great for those molecules that are close to their neighbors and smaller for those that are further away, it is seen that the natural period will vary through a considerable range as the active molecules move about, and at each instant there will exist in the substance molecules having all periods lying between certain rather wide limits. The absorption spectrum of the substance therefore consists of bands rather than of lines.[1]

When a molecule is dissociated by the action of the exciting light, the two parts, being electrically charged, will be more strongly attracted by the molecules of the solvent than was the original neutral molecule. Recombination of the separated ions is therefore more likely to occur when the latter are in the immediate neighborhood of the molecules of the solvent, *i. e.*, under conditions which make the period of the resulting vibrations longer, on the whole, than the period natural to the active molecules before dissociation. Since recombination can occur under a variety of conditions a wide range of wave-lengths will be represented in the luminescence spectrum; the latter also will consist of bands rather than of lines.

[1] Essentially this explanation of the broadening of spectral lines has been discussed in some detail by Galitzin, Wied. Ann. 56, p. 78, 1895.

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But on the whole the wave-length of the light emitted during luminescence will be longer than that of the exciting light. The same sort of thing will occur, although in less marked degree, even when the active molecule is itself electrically charged, as in the case of fluorescein. In this case, as well as in that first considered, it may even be that each of the two parts into which the active molecule is dissociated becomes a nucleus to which neutral molecules are attracted so that the ions become heavy aggregations of molecules. This is the assumption usually made regarding the production of ions in gases by the action of Roentgen rays, cathode rays, etc. If this is the real condition of affairs, the reasons for increased wave-length in the light emitted are still more evident.

It will be seen that this way of looking at the phenomena of photo-luminescence gives what might be called a mechanical explanation of Stokes' law. It does not lead us to expect, however, that Stokes' law will always be *exactly* followed. The luminescence spectrum and the absorption spectrum may overlap; in fact, it is to be anticipated that they will do so in the majority of cases. This is in agreement with the more recent experiments on this subject.[1]

Among the other experimental laws of photo-luminescence that are satisfactorily accounted for by the theory of Wiedemann and Schmidt may be mentioned the fact that the form of the luminescence spectrum is the same whatever may be the wave-length of the exciting light.[1] Light corresponding to any part of the absorption band may, if sufficiently intense, produce dissociation. But the manner in which recombination occurs will not depend in any way upon the wave-length of the rays by which the dissociation was produced.

Upon the basis of this theory it is clear also that we should expect no change in the form of the phosphorescence spectrum during decadence. The intensity of phosphorescence will depend at each instant upon the number of recombinations that occur per second, and will therefore diminish as the number of free ions becomes less. But it seems probable that the number of recombinations that occur under such conditions as to give light of a certain wave-length will still remain the same fraction of the whole

[1] Nichols and Merritt, PHYSICAL REVIEW, Vol. 18, p. 403, 1904.

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number. The case has some resemblance to that of the distribution of velocities among the molecules of a gas; if the total number of molecules in a given volume is diminished, the number having a given velocity will also diminish; but this number will still be the same fraction of the whole.

The simplest hypothesis regarding the law of recombination of the ions in a luminescent substance is that which has been applied to the case of ionization in gases.[1] Let the number of positive ions present per c.c. at any time t be n. The number of collisions between a positive and a negative ion will be proportional both to the number of positive ions and to the number of negative ions; and a certain fraction of these collisions will result in recombination. Since positive and negative ions are present in equal numbers we have

$$\frac{dn}{dt} = -an^2,$$

$$\frac{1}{n} = c + at \quad \text{where} \quad c = \frac{1}{n_0}.$$

Since the intensity of phosphorescence is proportional to the number of recombinations per second

$$I = kan^2 = \frac{ka}{(c + at)^2}.$$

This is one form of the expression originally proposed by E. Becquerel to express the decay of long time phosphorescence, and is the same law that was derived on the basis of entirely different theoretical assumptions by H. Becquerel.[2] As was shown in the first part of this paper the equation represents satisfactorily the results of our own experiments with Sidot blende.

In comparing our experimental results with the law just derived it was convenient to write the above expression in a different form: namely

$$\frac{1}{\sqrt{I}} = a + bt,$$

where

$$a = \frac{1}{n_0\sqrt{ka}}; \quad b = \sqrt{\frac{a}{k}}.$$

[1] Rutherford, Philosophical Magazine, Vol. 44, p. 422, 1897.
[2] Comptes Rendus, Vol. 113, p. 618, 1891.

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It is to be remembered that if I refers to the intensity at some particular part of the phosphorescence spectrum, k must be regarded as a function of the wave-length.

The fact that the experiments indicate a linear relation between the time and $I^{-\frac{1}{2}}$ has already been pointed out, and reference to the tables on pages 284–5 shows that the differences between the computed and observed values of t, which are usually small, are entirely unsystematic. It is possible to test the law still further by considering the values of the constants a and b. Except in the case of the last curve of Table I., the data refer to curves of decay for different wave-lengths, but with the same excitation. α and n_0 are therefore constant, while k depends upon the wave-lengths. It will be noticed that

$$\frac{a}{b} = \frac{1}{n_0\sqrt{k\alpha}} \cdot \sqrt{\frac{k}{\alpha}} = \frac{1}{n_0\alpha}.$$

This quotient should therefore be a constant for all curves taken with the same excitation and under similar experimental conditions. The values of the ratio a/b for the three curves of Table III. show considerable variation from equality, being 1.5, 2.0, and 1.7. The values of the ratio for the first three curves of Table I. are 1.73, 1.75 and 1.65. In view of the difficulty of maintaining constant conditions in the experiments on phosphoresence the agreement between these three values is highly satisfactory. As already stated the observations at 0.483 μ in Table II., probably on account of some experimental error, cannot be represented by the expression here considered, so that the value of a/b for this curve cannot be determined. But for the curves taken at 0.512 μ and 0.547 μ (Table II.) the quotient a/b has the values 2.32 and 2.43, respectively. Here, too, the agreement is all that could be expected.[1] Our results therefore afford strong confirmation not only of the conclusion reached in our last communication that all parts of the green band decay at the same rate, but also of the general theory of phosphorescence that we have used in deriving the law of decay.

The data permit still another test of the general theory, the result

[1] There is no reason why the values a/b for Table I. should be the same as those for Table II. or III. since the observations were made several weeks apart, and with no attempt to keep the intensity of the comparison source the same in the different cases.

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of which is less satisfactory. It will be remembered that in the case of the fourth curve of Table I. the exciting light was less intense than that used with the other curve for 0.512 μ. The observations for the fourth curve were made on the same day as those for the second curve, and although the former were made in the afternoon and the latter in the forenoon, every attempt was made to keep the comparison source the same in the two cases and to have all the other experimental conditions as nearly as possible constant. If we compare the two curves for 0.512 μ in Table I., we see that a and k have the same value for both, while n_0 is different. The constant b, however, is independent of n_0. This constant should therefore have the same value for both curves; in other words the straight lines obtained by plotting $I^{-\frac{1}{2}}$ should be parallel. As a matter of fact the values of b determined for the two curves are 0.045, for the second curve of Table I., and 0.052 for the fourth. The fact that the two values are unequal is shown in Fig. 37 by the lack of parallelism of the two lines A' and B'.

The law of decay derived upon the basis of the simple considerations outlined above, while representing the results of observation during the early stages of phosphorescence with surprising accuracy, can not be regarded as more than a first approximation to the correct expression. When the curve of decay is followed for several minutes instead of for several seconds a systematic variation is found from the linear relation between $I^{-\frac{1}{2}}$ and t. Experiments dealing with the long-time phosphorescence of Sidot blende and certain other substances will be described in our next paper.

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A METHOD OF CALIBRATING GAS METERS.[1]

BY FRANCIS GANO BENEDICT.

FOR physical or physiological experimenting, gas meters in which the revolving metal drum is partially immersed in water are frequently used. One of the best forms is that made by S. Elster,[2] of Berlin. The drum of this meter is connected by gear wheels to dials which register the quantity of gas passing through it. This type of gas meter is much more accurate than are the so-called "dry" meters, but its readings require numerous corrections, such as those for temperature, barometric pressure, tension of aqueous vapor, tension of the gas in the meter, rate of flow and finally, for possible mechanical inaccuracies in the registering device of the meter itself.

Inasmuch as all meters are subject to variations in mechanical accuracy and especially to the variations due to the rate of flow, it is necessary to calibrate each meter and compare the readings obtained from the dials with the true volume of gas passed through the meter. In order to calibrate accurately, therefore, a mechanical gas meter, it is necessary to know with great exactness the true volume of gas which is passed through it.

The usual method of ascertaining the true volume of gas is by means of some form of aspirator, from which the air can be forced through the meter or into which it can be drawn. The use of an aspirator is, however, unfortunately subject to considerable error. In the first place, there may be marked changes in the temperature of the aspirator itself, especially if it be of any considerable size. As a matter of fact, this possible error has restricted the size of aspirators to such an extent that it is rare that an aspirator containing over ten liters can be used advantageously. Consequently, the

[1] Contribution from the Chemical Laboratory of Wesleyan University.

[2] For a description and diagrams of the construction of the Elster type of meter see v. Flügge, Hygienische Untersuchungsmethoden, Leipzig, p. 351, 1881.

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total volume of air passed through the meter and used for checking its accuracy may not exceed ten liters whereas the meter itself may be designed to record several thousand liters. Furthermore, in spite of the fact that the Elster meter is so devised as to require a minimum pressure to rotate the drum and dial, it is a fact that at the beginning of each calibration there is a period when there is a gradually increasing pressure of the gas inside the system, and at the end, a similar falling off in pressure. These two inequalities in large measure compensate, but on so small a volume as ten liters they may result in an appreciable error.

In this laboratory, an Elster meter is made use of in determining the carbon dioxide and water content of the residual air inside a large respiration chamber containing about 5,000 liters. For this purpose a sample must be drawn in not more than three or four minutes which should not exceed ten liters. As a result the analyses made on this sample must be multiplied by a very large factor, *i. e.*, 500, in order to give the true amount of carbon dioxide and water vapor inside the respiration chamber, and this necessitates great care in the calibration of the meter. While undoubtedly an aspirator method when accurate in all its details[1] would give a calibration which would be perfectly satisfactory for our purpose, another method for ascertaining the true volume of gas passed through the meter has been used in this laboratory.

In principle the method is as follows: Oxygen from a weighed cylinder of the highly compressed gas is allowed to pass through the meter. The volume of the issuing gas is computed from the loss in weight in the cylinder and the known weight of a liter of oxygen, making due allowance for the barometric and thermometric conditions of the experiment.

It is possible to obtain in the market, small steel cylinders filled with highly compressed oxygen.[2] The oxygen is not absolutely pure, containing besides three to seven per cent. of nitrogen, small

[1] A special form of aspirator (ten liters), provided with protection against sudden temperature fluctuations, has been devised by N. Zuntz. (See Untersuchungen über den Gaswechsel und Energieumsatz des Radfahrers. Leo Zuntz, Berlin, p. 8, 1899.

[2] Several hundred of these cylinders have been used in this laboratory during the past three years. They are obtained from the S. S. White Dental Mfg. Co. at Prince's Bay, Staten Island, N. Y.

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amounts of water vapor and carbon dioxide, but if the gas leaving the cylinder is conducted first, through soda lime, and second, through sulphuric acid, the gas leaving the exit tube of the apparatus will consist of pure oxygen and nitrogen, the proportions of which can be readily found by the usual gasometric analyses.

The cylinders contain ten cubic feet (283 liters) of gas and weigh when filled with gas about fifteen pounds (seven kilograms). A balance at once large enough to support a load of ten kilograms and sensitive enough to detect small differences in weight is made in Germany by Sauter.[1] The balance can be considerably overloaded, so that it is capable of weighing the oxygen cylinder and purifying attachments with a total weight of somewhat more than ten kilograms to within ten to twenty milligrams. Since the weight of one c.c. of oxygen is 1.43 mgms., the total volume of gas leaving the cylinder can be computed from the weight to within 7 to 14 c.c. In one of these steel cylinders there are compressed 283 liters and it is thus seen that it is possible by this means to measure the volume of 283 liters of gas to within 30 c.c., an accuracy that cannot be obtained by any other means of securing so large a known volume of gas with which the writer is familiar.

The details of manipulation are as follows:

An oxygen cylinder to which the regular connection is attached is supplied with two U-tubes, one containing soda lime and the other sulphuric acid, connected in series and with the oxygen cylinder. On opening the valve the oxygen flows through the two tubes and is thereby deprived of its carbon dioxide and water. Inasmuch as the valves on the oxygen cylinder are not so constructed as to control the enormously high pressure of 1,800 pounds with the greatest fineness, it is best to introduce some device for preventing the loss of gas in a sudden rush through the U-tubes. This result has been found to be obtained by placing a rubber bag, *i. e.*, a common foot-ball bladder, in a T-tube between the yoke connection and the first U-tube. The oxygen cylinder with its fittings is then weighed,

[1] Three such balances, obtained through the Bausch and Lomb Optical Co., are in use in this laboratory, the smallest one weighing to ten kilograms with a sensitiveness of less than ten milligrams. This balance in a glass case cost delivered in Middletown, Conn., duty free, but about sixty dollars.

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using a counterpoise and ordinary brass weights. The purifying devices are attached directly to the cylinder by means of stout rubber bands and are weighed with the cylinder.

A rubber tube leads from the sulphuric acid U-tube and conducts the dry, carbon-dioxide free gas into the meter which is to be calibrated. From 10 to 283 liters of gas may be passed through the meter and the readings on the dial carefully recorded. By means of the valve on the oxygen cylinder and the rubber bag, it is possible to maintain a very constant flow of gas at any desired rate. It has been repeatedly proved that with the Elster meter, the gas passing through at the rate of three liters per minute is completely saturated with water vapor and consequently the tension of this water vapor may be correctly determined by knowing the exact temperature of the gas. Experiment has shown that the temperature of the gas in the meter is that of the water in the meter. A thermometer graduated in tenths of a degree and read to hundredths is inserted in the meter and gives this temperature. The barometric pressure is read at the beginning and the end of the experiment and the tension of the gas in the meter is noted by a water manometer attached to it. From the data regarding barometric pressure, temperature of the meter, tension of the gas in the meter and loss in weight of the oxygen cylinder, the true volume of gas passing through the meter may be computed and compared with the reading on the dial.

In the computation of the true volume of gas issuing from the cylinder the following data are used :

Weight of one liter of oxygen under standard conditions of temperature and pressure and at the latitude of 45° = 1.42900.[1] This corrected for the value of g at Middletown (41° 34″) becomes 1.42853 grams.

In calculating the weight of one liter of atmospheric nitrogen at Middletown the ratios between the weights of oxygen and nitrogen as found by the three observers, Von Jolly, Leduc and Rayleigh,[2]

[1] Morley, Smithsonian Contributions to Knowledge, 980, p. 111, 1895.

[2] The values found by these three observers are given by Rayleigh and Ramsay in their monograph, "Argon. A new constituent of the atmosphere," Smithsonian Contributions to Knowledge, 1033, p. 14, 1896.

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are compared with the weight of one liter of oxygen at Middletown in the following manner:

$$\text{Von Jolly,} \quad 1.42853 \times \frac{1.25819}{1.42971} = 1.25715 \text{ grams}$$

$$\text{Leduc,} \quad 1.42853 \times \frac{1.25709}{1.42910} = 1.25659 \text{ grams}$$

$$\text{Rayleigh,} \quad 1.42853 \times \frac{1.25718}{1.42952} = 1.25631 \text{ grams}$$

$$\text{Average of 3} = 1.25668 \text{ grams}$$

It is thus seen that one liter of atmospheric nitrogen under standard conditions of temperature and pressure and corrected for gravity at Middletown weighs 1.25668 grams.

The loss in weight of the oxygen cylinder gives the weight, not of pure oxygen, but of the weight of oxygen containing a known percentage by volume of nitrogen. It is possible to compute the weight of one liter of gas of the composition represented by that in the cylinder by means of the above factors and by means of the percentage composition of the oxygen as determined by the gasometric analyses.

An example of this calculation is here given: Cylinder No. 38367 contained 96.144 per cent. oxygen and 3.856 per cent. N by volume.

96.144	liters of oxygen	$\times$ 1.42853 =	137.34 grams.
3.856	" " nitrogen	$\times$ 1.25668 =	4.85 grams.
100	" " mixture weighs		142.19 grams.

Or 1 liter weighs 1.4219 grams.

Consequently the loss in weight of the cylinder divided by the weight of one liter of the mixed gases gives the volume of the gas that has been removed from the cylinder.

The meter was calibrated under conditions similar to those in which it is ordinarily used. Air was forced through the meter at a rate of about 3 liters per minute. After leaving the meter it was caused to bubble through concentrated sulphuric acid. Thus there was normally a pressure on the air in the meter corresponding to the pressure required to force 3 liters of air per minute through the layer of sulphuric acid in the drying bottle. This pressure was measured by a water manometer and was not far from 80 mm. of water.

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A sample calibration follows :

Reading of meter at end	= 93.374 liters
" " " " start	= 2.492 liters
	90.882 liters.

Temperature of Meter 20.13.° Manometer = 80 mm. water = 5.88 mm. Hg.

Barometer at begin. (4.54 P. M.)	= 754.30 mm.
" " end (5.27 P. M.)	= 754.20 mm.
Average	= 754.25 mm.
Manometer correction	= 5.88 mm.
Sum	= 760.13 mm.
Tension water vapor at 20.13°	= 17.50 mm.
	742.63 mm. corrected pressure.

$$90.882 \times \frac{1}{1 + a20.13} \times \frac{742.63}{760} = 82.695 \text{ liters.}$$

The weight of the oxygen cylinder at the beginning of the calibration was equal to that of

The counterpoise	+ 2,712.25 grams.
At end "	+ 2,594.25 grams.
Weight of Oxygen + Nitrogen	= 117.30 grams.
117.30 ÷ 1.4219	= 82.496 liters.

Consequently the meter reading is slightly higher than the true value, the correction factor being obtained from the ratio between 82.695 and 82.496. All meter readings obtained at the rate of flow and pressure conditions observed here, therefore, are to be multiplied by the factor 0.9976.

In conclusion I wish to acknowledge my indebtedness to Miss Charlotte R. Manning, of this laboratory, for her assistance in conducting the tests of this method.

MIDDLETOWN, CONN.

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ON THE GEYSER IN ATAMI, JAPAN.

BY K. HONDA AND T. TERADA.

THE remarkable phenomena of the periodic eruptions of geysers have attracted the attention of many observers. Mackenzie[1] observed the Great Geyser of Iceland in 1811 and tried to explain the phenomenon. But his theory proved unsatisfactory. Bunsen[2] visited the same geyser in 1847 and proposed his well-known theory of the vertical pipe. Müller[3] constructed a model after Bunsen and showed that it worked periodically if two portions of the vertical pipe be heated. This theory, however, is not free from objections. Contrary to Bunsen's view, O. Lang[4] considered the seat of eruption to lie at a great depth below the vertical pipe, the water in which acted as a valve for the enclosed vapor. Models given by J. Ziegler[5] and G. Wiedemann[6] explain the phenomenon of the geyser from a similar point of view. Other models by J. Petersen, A. Andreae and others[7] do not differ much in principle from those just referred to. The experimental investigations of Andreae[8] and H. Ebert[9] show

[1] Mackenzie, Travels in Iceland, 1811.

[2] Bunsen, Physikalische Beobachtungen über die hauptsächlichsten Geysir Island, Gehlers Physikalisches Wörterbuch (2 Auflage), LXXII.; Pogg. Ann., 72, 1847.

[3] Müller, Lehrbuch der Kosmischen Physik, Braunschweig, 1894, S. 619.

[4] O. Lang, "Ueber die Bedingungen der Geysir," Göttinger Gelehrten Nachrichten, 1880, S. 225.

[5] J. Ziegler, Vorträge des phys. Vereins in Frankfurt a. M., 1872, demonstrated by Dr. Nippoldt.

[6] G. Wiedemann, "Ueber einen Apparat zur Darstellung der Erscheinungen der Geysir," Ann. der Physik und Chemie (2), XII.

[7] J. Petersen, "Darstellung der Geysir Erscheinungen," Neues Jahrbuch für Mineralogie, Geologie and Paläontologie, 1879, II.

A. Andreae, "Ueber einen künstliche Nachbildung der Geysirphänomene," Ibid., 1893, II.

K. Antolik, Zeitschrift f. d. Phys. u. Chem. Unterr., 1890–91.

A model given by A. C. Munby, Nature, 65, p. 247, is of a somewhat different principle.

[8] Andreae, loc. cit.

[9] H. Ebert, "Versuch mit dem G. Wiedemannschen Geysirapparate," Annalen d. Phys. u. Chem. (2), LXIII.

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that by properly modifying different parts of the models, several types of natural geysers can be imitated. The latter, however, remarks that such a simple theory is not able to explain all the diversities in the manner of eruption observed in numerous geysers in Iceland, North America and New Zealand.

Different from other geysers, the geyser of Atami in the province of Izu is characterised by the regularity of the eruption, which consists in alternate projections of hot water and steam, usually five times in succession. The water projected does not return to the orifice as it does in several other geysers. The orifice, which originally opened vertically upward, has been covered by a heap of stones to prevent the dangers caused by the eruption. At present three orifices are exposed, among which one is distinguished as the principal opening. Besides, there is another mouth hidden underground ; the water projected by these orifices is distributed to several bath-houses by conduits. The water is of a strong saline taste, containing about ½ per cent. of sodium chloride, *i. e.*, about one fifth of that contained in the sea water. The mouth of the geyser is not far from the sea coast and about 22 m. above the sea-level.

The eruption occurs usually five times in a day and night. During the time of repose, we see only a small quantity of steam rising from the mouth. As the time of the eruption approaches, a rumbling sound is heard underneath. The boiling water appears just inside the mouth. It soon retires and again appears. This state continues for about three quarters of an hour. Next a small quantity of hot water flows out intermittently. This is followed by an intermittent stream of moderate quantity with a longer period. The activity soon attains its maximum. A torrent of hot water gradually increasing in force is torn into a violent splash and projected with a great velocity by steam which gradually increases with the diminishing water. When the roaring sound of steam reaches the maximum, the water almost disappears. The steam now diminishes and is soon followed by the second gush of water. After these states have been repeated five or six times, the activity ends with the last steam which gradually subsides into an inconsiderable amount as seen at the beginning. It takes above two hours from the beginning to the last stage of the eruption. The time of repose

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is a little less than three hours on the average. These regular recurrences are often interrupted by an abnormal outburst, called *nagawaki*, at which the water and steam come out incessantly for above twelve hours and after which a long repose follows as a rule. In years rich in this anomaly it occurred almost monthly, whereas in the last few years only once or twice.

Our excursion to Atami was undertaken to make detailed observations as to the manner of eruption and if possible to get an insight into the internal mechanism of the geyser. Arrangements were contrived to keep records of the manner of each successive eruption.

A pendulum consisting of a brass rod and a heavy lead ball was hung before the principal orifice. The water and steam, projected nearly horizontally, deviate the pendulum by the impulsive pressure. The motion of the pendulum was transmitted by a cord and pulley to a recording pen guided by two vertical pillars with grooves, in which roll two friction-wheels attached to the penholder. The vertical displacement of the pen was recorded on a cylinder making one revolution every two hours. The pendulum was afterward removed to a position where the impulsive action of vapor and splash was shielded off and the flow of water only could be recorded.

To record the manner in which the steam is ejected, an arrangement was used which was nothing more than an air-thermograph. A small cylinder of sheet zinc was introduced into a mouth neighboring to the principal orifice, where it was possible to find a position such that the bulb was exposed to the heating of the steam only. This orifice, being a smaller branch of the main one, could be considered as representing the main one on a reduced scale. The bulb was connected by a fine copper capillary tube to one of the arms of a U-tube containing mercury. The motion of the mercury meniscus in another arm was recorded on a cylinder by a pen mounted on a float on the mercury and guided by two vertical pillars with grooves and two friction-wheels attached to the penholder. To determine the temperature of the water and steam a maximum thermometer was used.

To take continuous records of the exact time of eruption, and also the general manner of each eruption, a mercury tide-gauge,

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constructed after Mr. Nakamura's design,[1] was used. The lead pipe of the instrument was inserted to the neck of the geyser. The pressure of the projected water at the neck during each eruption was recorded on a cylinder revolving once every 24 hours. The automatic records of daily eruptions have been taken during the last two years.

In the following lines, a brief account of our results of observation is given.

I. Ordinary Eruption.

An ordinary eruption consists of three distinct series, termed conventionally the first, the second and the third, differing in period and force and succeeding one another very regularly. Fig. 1 is a reproduction of one of the records obtained by our pendu-

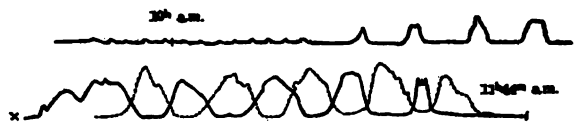

Fig. 1.

lum recorder. The abscissa represents the time, and the ordinate the deflection of the pendulum by the pressure of water. The dotted line shows the velocity of the steam obtained by our air-thermograph. The first series, which begins the outburst, consists of a small quantity of water appearing with an average period of 1 minute and 40

Fig. 2.

seconds. After this intermittence has been repeated a score of times the second series follows. A moderate quantity of water comes out three or four times with a mean period of six minutes. The water increases in quantity and force till at last the third or

[1] S. Nakamura, Proceedings of the Tokyo Physico-Mathematical Society, Vol. I., No. 15, p. 123, 1902.

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principal series sets in. On the first outburst of the third series we see very often the superposition of the last one of the second series. The third series is to be distinguished from the previous series by its violence and the quantity of water and steam. The sequence of the water and steam occurs usually five or six times with a mean period of about 11 minutes. Fig. 2 is a record obtained by the mercury tide-gauge, and shows regular periodic sequence of eruptions with a mean period of 24/5 hours.

II. ABNORMAL ERUPTION; NAGAWAKI.

The first *nagawaki* recorded by our arrangement began at 4:30 A. M. on January 14, 1905, from the fourth eruption of the third series. During two or three days before the *nagawaki*, the period of successive eruptions seems to have been slightly diminished; but in such a degree that may be found not seldom in our records without leading to either *nagawaki*, or anything extraordinary. The *nagawaki* began, as it were, almost suddenly in the midst of an ordinary eruption. The flow of hot water continued without interruption, gradually decreasing in quantity and mixed with steam. At 7:40 P. M., it came to a sudden repose; at 2:40 A. M. on the 15th, an intermittent flow of hot water resembling the second series of an ordinary eruption began and continued for about three hours. After a repose of four hours ordinary eruptions at last set in, but with the period remarkably shortened and the activity strikingly reduced. The number of eruptions per day was ten, a remarkable contrast to the ordinary frequency of five. The frequency decreased afterward very slowly with the time, and recovered its original value after the lapse of about a month.

The second *nagawaki*, which occurred on May 26, was quite similar to the previous one in its general aspects, though it took place in conjunction with the extraordinary decrease of the general activity.

It is an interesting coincidence that the two *nagawakis* of January and May began at the same phase of the ordinary eruption at nearly the same hour of day, and that a center of low atmospheric pressure was approaching from the Pacific in each case.

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III. Influence of Atmospheric Pressure.

Examining our records of long observation, we found a remarkable fact that low atmospheric pressure *retards* and high atmospheric pressure *accelerates* the eruption of the geyser. This curious fact may be seen from Fig. 3. Times of the successive eruptions are plotted as the ordinates corresponding to each day which is laid off as abscissa; corresponding points for successive days are connected into five broken curves (*b*)–(*f*). Curve (*a*) represents the daily change of the mean atmospheric pressure. The probable cause of the strange coincidence would be given later.

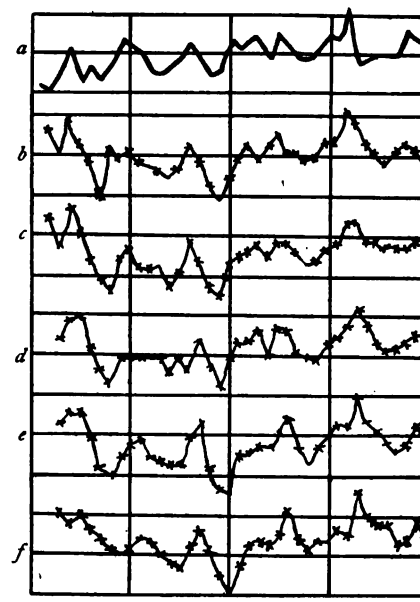

Fig. 3.

IV. Temperature of Hot Water During Eruption.

A maximum thermometer was placed about 1.5 m. inside theorifice and the temperature has been read daily since last April. It was found that the temperature at this depth was almost invariably 103°–104° C. At the orifice, however, it was about 100° C., indicating a rapid cooling of the hot water. Hence it may easily be conjectured how hot the underground water would be at a depth of some ten meters.

V. Velocities of Water and Steam.

The pressures of water and steam upon the bob of a special pendulum arrangement were recorded on the cylinder, and estimated afterward by the substitution of known weights. The total pressure upon a sphere is known to be approximately equal to one half of that upon a circular disk of the same diameter. Hence

$$p = \frac{\pi r^2 \rho v^2}{2}, \quad \text{or} \quad v^2 = \frac{2p}{\pi r^2 \rho},$$

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where p is the pressure, r the radius of the bob, ρ the density and v the velocity of water or steam. For the water we obtained, at the mouth,

$$v = 1.5\text{–}2.0 \text{ m. per second,}$$

and for the steam

$$v = 18\text{–}24 \text{ m. per second,}$$

the velocities varying within the limits according to the phase of each eruption. In this calculation, we took for the value of ρ the density of saturated vapor under ordinary atmospheric pressure.

VI. Quantities of Water and Steam.

For the rough estimation of the quantity of water thrown out in an eruption, we measured directly the amount supplied to a number of tanks and calculated the total from the sections of several conduits. The quantity thus estimated amounts to 45 cubic meters.

The rough estimation of the quantity of steam was carried out in the following way:

Let the quantity of steam be denoted by Q. Then

$$Q = \int Sv\rho dt,$$

when S is the area of the orifice. If V be the ordinate in the curve representing the relation of velocity of steam to time, obtained by our special thermograph above referred to, we may put

$$v = kV, \quad \therefore \quad Q = S\rho k \int V dt.$$

Since v was determined by the pendulum experiment, and the corresponding V from the thermograph curve, k can easily be known; by calculation, it was found to be 500. S was estimated to be 200 cm.^{2}; for an instance, we obtained

$$\int V dt = 6{,}500, \quad \therefore \quad Q \doteqdot 500 \, kg,$$

the number must be considered as giving only the order of magnitude.

VII. Extraordinary Decrease of Activity.

During the course of the last few years, several wells have been bored in this district. Most of them give a moderate quantity of

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hot water only by pumping. Since the last year, the number of wells was greatly increased, amounting to about twenty in all. Sawaguchi's well, bored on March 27 of this year, burst out with great violence, throwing up a column of hot water about 8 m. high. On May 22, another one, Yonekura's well, of greater activity, has been opened within a few hundred meters of the geyser, giving hot water at a rate of 310 cubic meters per day. Two days afterwards another one, Hignchi's well, of not much less activity, was bored. After the boring of the Sawaguchi's, a slight decrease in the frequency of the geyser was observed; on May 20 it was reduced to 4.4, though the force of each eruption presented no appreciable change. After the boring of the other two the frequency remarkably decreased; it was 3.6 on May 26. Moreover, the first and second series of each eruption became considerably longer and the principal series was considerably lessened in force. After the *nagawaki* of May 27, the frequency was temporarily increased; but on June 11, it fell again to 3.2. As shown in Fig. 4, the first and second series lasted for three and a half hours and

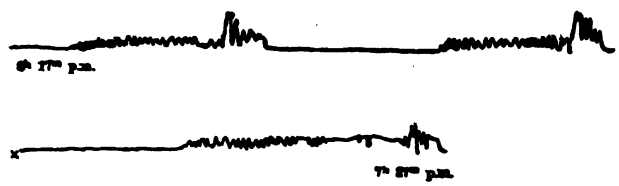

Fig. 4.

the third was reduced to only three weak eruptions. Consequent decrease in the quantity of hot water caused trouble to several bathhouses supplied by the geyser, and therefore the above three wells were all stopped — Yonekura's on June 12, Sawaguchi's on the next day and Higuchi's on July 12. The frequency of eruption has gradually increased since then, and in the middle of August, it attained 4.5 which is yet somewhat short of the original value. As for the mode of each eruption, it has quite recovered in force.

VIII. Level Change and Temperature of Wells.

Level change of two wells near the geyser were recorded by means of Honda's limnimeter. Nomura's well, which is within 200

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m. of the geyser and quite high above the sea level, shows a regular up and down motion corresponding to the eruption and repose of the neighboring geyser. Effects of the tidal and atmospheric pressure are also recognizable, but not very remarkably. (Fig. 5.) The

Fig. 5.

temperature of the water of this well is 50°–60° C. In Suzuki's well, which is more remote from the geyser than Nomura's, the effect of the geyser is not observed, but the level rises and falls with the tide. (Fig. 6.) The head of the water is 22 m. above the sea

Fig. 6.

level. Temperature measurement with a maximum thermometer was made in Abo's well, which is situated in the midway between the geyser and Yonekura's well. The results are tabulated as follows:

At the surface of water,	62°.0 C.
23 m. below,	95°.5
28.5 m. "	98°.3
29.7 m. "	104°.7
31.0 m. "	118°.2

Thus, a remarkably high temperature was found to exist in the surface layer of the district.

IX. Explanation of the Phenomena.

Existing theories on geysers fail to explain the exact manner of eruption of the geyser of Atami. After a series of experiments with several forms of models, we arrived at a theory which we hope may fairly explain the phenomena of the geyser in question.

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Referring to Fig. 7, *A* is a cavity lying in a considerable depth; *a* is the vertical pipe and *b* a canal which supplies the water to *A*. We conceive a side canal *c* intermediate between *A* and *a*, which leads to a second cavity *C*, not shown in the figure. The temperature of the water in *a* and *c* is supposed to be lower than the corresponding boiling point. Water in *A* is heated by the wall of the cavity, the temperature of which is supposed to be decidedly higher than the boiling point at the depth. The source of the heat is probably to be attributed to the hot water and steam running through numerous veins and canals extending in the depth of the district. When the tension of the vapor in the cavity attains a critical value, the water is thrown off and then the steam follows. When a certain amount of steam is given off, the pressure in the neck is reduced to such a degree that the water flows in from the side canal and stops the eruption momentarily. Soon the downward pressure of the water column is overcome by the tension of vapor and the second gush follows. These eruptions are repeated several times, till the vapor pressure is so reduced as to admit the comparatively colder water from the feed canal *b* and also from *c*. Thus the activity is quenched for a while till the next eruption begins. A model (Fig. 8) constructed according to this view, worked very satisfactorily. The manner of eruption was imitated in many details.

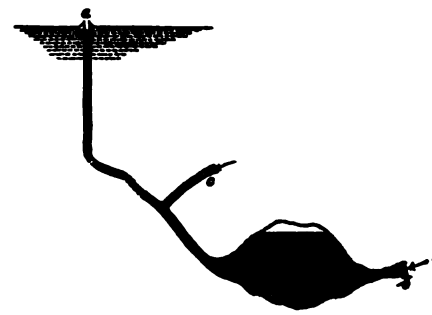

Fig. 7.

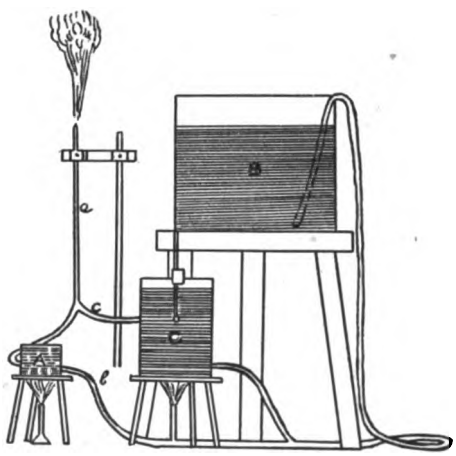

Fig. 8.

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The number of intermittences in an eruption increases with the temperature of the water in *c*.

The phenomena of *nagawaki* may be explained partly by the supposition that the underground temperature is raised above its normal value and so the temperature of the cavity *C* becomes higher than the ordinary case. If the temperature of the cavity *C* in our model be raised to a certain value, the eruption corresponding to *nagawaki* begins. It resembles the actual one even in some details. The cause of this occasional change of temperature is probably the change of the subterranean volcanic activity which keeps the underground temperature in this district considerably above the boiling point of water.

The fact that the frequency of eruptions immediately after *nagawaki*, is nearly doubled, may partly be explained, if we consider that the temperature of the heating cavity was raised during the course of the *nagawaki* by the incessant flowing of superheated water from a great depth. It may be added as a very suggestive fact that if in our model, a quantity of air be blown into the heating cavity, the frequency of eruption increases at first remarkably and gradually decreases with the gradual expulsion of air by successive eruptions; even the weakness of activity in the actual case is imitated with great faithfulness. During a few hours after *nagawaki*, the cavities as well as the canals leading to the orifice remain drained out, so that it is possible that air or other gases may enter into the cavities and cause the increased frequency of the eruption.

It is a common fact of observation that the temperature of some ordinary hot springs rises with low atmospheric pressure. This is undoubtedly due to the increase of flow due to the enhanced circulation of water caused by the reduction of the pressure. If in the supposed heating cavity of the geyser, the interchange of water due to the slow circulation through numerous veins and fissures (not shown in the figure), be accelerated by some cause, the time required for the sufficient heating for eruption must necessarily be prolonged. This consideration seems to explain partly the influence of atmospheric pressure on the period of eruption above mentioned. Again, the possible influence of well-boring on the geyser, may be explained on the same basis. Such a well may increase the circu-

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lation of underground water in its vicinity and result in the retardation of the eruption of the geyser in a similar manner. Moreover, it is quite natural that the hot water should find its easier vent through a new passage opened with a less resistance, at the expense of the quantity originally given out by the old one alone. The prolongation of the first and second series of an eruption, suggests the slowness with which the pressure in the heating cavity approaches the critical value. The careful investigation of the variation of the frequency in connection with the boring and stopping of the wells, leads us to the strong belief that the striking coincidence of the well-boring and the decrease of the activity of the geyser, is a necessary, and not an accidental one. If the frequency of eruption does not yet quite attain its former value long after the stopping of the wells, we need not wonder at all, since some irreversible change in the subterranean mechanism might have happened during the period of the anomaly.

PHYSICAL LABORATORY,
IMPERIAL UNIVERSITY, TÔKYÔ,
December 28, 1905.

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ON AN EMISSION OF NEGATIVELY CHARGED PARTICLES PRODUCED BY CANAL RAYS.[1]

BY L. W. AUSTIN.

THE work described in the following paper was undertaken for the purpose of studying the possible secondary radiations produced by the impact of the canal rays on a metal. Since it is known that the canal rays consist of positively charged particles of molecular dimensions travelling with a velocity sometimes exceeding 10^8 cm./sec.,[2] it seemed probable that they might give rise to reflected positive rays analogous to the reflected cathode rays studied by several physicists,[3] and perhaps also to an emission of negative particles.

The tube used in the work is shown in Fig. 1. It was divided into two parts *A* and *B*. The part *A* was 7 cm. long and 2.5 cm. in diameter. *B* was 7 cm. in diameter and was separated from *A* by the system of brass diaphragms *d* with openings 2 mm. in diameter. The aluminum electrode *e* formed the anode while the front of the diaphragms served as cathode. The canal rays passed backward through the openings in the diaphragms into the observation space *B*, which was lined with fine brass netting. This with the diaphragms was connected to earth, thus forming an enclosed space practically free from the direct influence of the discharge. In looking for the reflection of the canal rays the following arrangement was used. A small brass cylinder *C*, 1.5 cm. in diameter and 1 cm. long, closed except for an opening 4 mm. in

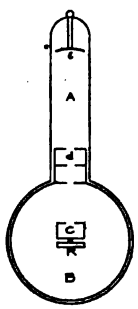

Fig. 1.

[1] Read before the Washington Philosophical Society, February 10, 1906.

[2] W. Wien, Wied. Ann., Vol. 65, p. 440, 1898; Ewers, Wied. Ann., Vol. 69, p. 167, 1899; Austin, Bulletin of Bureau of Standards, Vol. 1, p. 439, 1905.

[3] Goldstein, Wied. Ann., Vol. 15, p. 254, 1882; Campbell Swinton, Proc. Roy. Soc., Vol. 64, p. 377, 1899; Starke, Wied. Ann., Vol. 66, p. 49, 1898; Ann. d. Phys., Vol. 3, p. 75, 1900; Austin and Starke, Ann. d. Phys., Vol. 19, p. 271, 1902.

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diameter in the front, was fastened to a brass spindle. To the other side of the spindle was attached a brass disk R, 1.5 cm. in diameter. The spindle passed up through a ground glass joint and was connected to earth through a D'Arsonval galvanometer giving one division for 2.3×10^{-9} amp. This was shunted so as to have a lower sensibility during most of the work. The spindle could be turned so that the canal rays could be made to enter the cylinder C or strike the reflector R. In case the rays entered the cylinder all of the positive charges conveyed by them were caught and conducted to earth through the galvanometer. When the reflecting disk R was turned toward the rays the reflected portion would rebound and only the charges carried by the absorbed portion would pass through the galvanometer to earth. The difference in the currents indicated by the galvanometer in the two cases would represent the reflected portion of the rays.

The current for the tube was supplied by a motor-driven electrical machine with four moving plates capable of generating about 0.0003 amp. when driven at full speed. The amount of current could be varied at will by changing the speed of the machine. The difference of potential between the electrodes of the tube was measured by means of a Braun electrometer having a range of 500 to 10,000 volts. The vacuum was produced by a motor-driven Geryk oil pump.

The first observations showed that the reflection of the canal rays was entirely masked by a secondary negative emission, for the reflector current was found to be larger than the cylinder current.

As the work progressed it became evident that there were irregularities in the phenomenon of a very puzzling character. It was found that from time to time the ratio of reflector current to cylinder current varied between rather wide limits, and that these variations did not depend as far as could be observed either on the amount of current flowing or on the degree of vacuum and difference in potential between the electrodes. These irregularities have made it impossible to carry out the work with the same quantitative exactness as in the case of the cathode rays.

Irregularities have also been observed by Wien[1] in his determi-

[1] W. Wien, loc. cit.

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nation of the ratio e/m for the canal rays, and it seems possible that they may arise in both cases at least in part from common causes. As an explanation of Wien's results, J. J. Thomson has supposed that perhaps some of the positive particles have their charges neutralized by taking on negative electrons as they pass through the gas, and that they again become ionized when they strike against a solid and are thus able to produce fluorescence. If we suppose that such neutral particles are also capable of producing the negative emission we have a possible explanation of our irregularities, for the presence of these neutral particles could not in any way be discovered in the cylinder while they would produce a difference in the reflector current. Another difficulty in quantitative measurements with canal rays lies in their great absorption in thin layers of foreign substances on the surfaces struck by them.[1] Notwithstanding these difficulties observations made on the same day and without introducing air into the tube generally agreed within a few per cent.

If we call the galvanometer current from the cylinder C and from the reflector R, $(R - C)/C$ will represent the ratio between the emitted negative particles minus the reflected positive particles and the positive particles producing them. In Table I. are given the mean values of series taken on three different days. Observations were

TABLE I.

Discharge P. D. Volts.	Galvanometer Deflections. 10^{-7} amp.		$\frac{R-C'}{C}$
	C	R	
7,000	78	114	0.46
7 000	102	146	.43
6,000	77	109	.42

[1] In this connection the following experiment was carried out: Two brass reflectors were carefully polished and cleaned with alcohol and then fastened to the two sides of the spindle in the tube. When struck by the canal rays both gave almost identical galvanometer deflections. One of the reflectors was then removed and rubbed over with the thinnest possible film of pump grease. When the reflectors were again compared the greased one gave a galvanometer deflection of only 0.5 cm., while the bright one gave 18 cm. When the machine was reversed so that cathode rays struck the reflectors it was found that the grease film was almost without effect and that the two deflections were practically identical. Even after rubbing the greased reflector as clean as possible with a dry flannel cloth, it still gave only about half the full deflection for the canal rays.

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also made on other reflectors than brass. Cu gave practically the same results, Pt a larger relative negative emission and zinc a smaller one. But as observations with external E.M.F. in the galvanometer circuit showed that the conductivity in the space exposed to the canal rays was very high, so that a difference of potential of one volt between the reflector and earth produced a deflection amounting to a large fraction of the total effect due to the caanl rays, it was not thought best to put too much weight on these observations in which different metals were immersed in the conducting gas. For in this case it seems possible that the two metals would develop differences of potential as when immersed in an electrolyte.[1]

Since it is known that the negative emission produced when cathode rays strike a metal increases rapidly as the angle of incidence increases,[2] observations were made to determine whether this was also true in the present case. As the spindle bearing the reflector could be rotated it was possible to cause the canal rays to strike at any desired angle.

Table II. shows a set of these observations. It is seen that the galvanometer current increases rapidly as the angle of incidence increases, being more than 40 per cent. greater at 70° than at 0°.

TABLE II.

Angle of Incidence.	Galvanometer Deflections. 10^{-7} amp.
0°	156
40	170
60	196
70	223

And if we assume that the increase is entirely in the emission the difference amounts to about one and one half times.

In order to still further establish the existence of the negative emission and observe it directly the following arrangement was adopted: A cyclinder was constructed with the base insulated from the remaining portion by a hard rubber ring as shown in Fig. 2. Either part could be connected to earth through the galvanometer while the other was earthed directly. Any negative particles sent

[1] S. Arrhenius, Wied Ann., Vol. 33, p. 638, 1888.
[2] Austin and Starke, loc. cit.

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out from the base when struck by the canal rays were caught by the part a and could be detected by being led to earth through the galvanometer. When the experiment was performed it was found as was expected that while the base b gave a positive deflection as before, the part of the cylinder a showed a negative current. Table III. gives the mean value of three sets of observations taken on

TABLE III. (See Fig. 2.)

Discharge P. D. Volts.	Galvanometer Deflections. 10^{-7} amp.		$\frac{a}{b-a}$
	b	a	
4,000	+ 6.8	−1.9	0.38
"	7.5	2.2	.41
"	18.0	5.6	.42

different days. The ratio of negative emission minus reflected positive particles to canal rays is now expressed by $a/(b - a)$ and the agreement with the results of Table I. is good.

Besides the Volta effect already mentioned there were two other possible spurious causes of the phenomenon, namely the presence of cathode rays mixed with the canal rays due to oscillations in the circuit and the action of ultra-violet light coming through the diaphragms from the discharge portion of the tube. As a magnetic field in the observation space strong enough to divert any cathode rays from the reflector had no effect on the emission, and as all action in the observation space ceased when the cathode rays in the discharge tube were diverted so that the canal rays did not pass the diaphragms these possible sources of error were considered eliminated.

The velocity of the new emission seemed to be a question of considerable interest, and accordingly attempts were made to determine it approximately by the method of magnetic deflection. In the first experiment a brass plate p, 1.5 cm. long and 1 cm. wide, insulated from the spindle was placed 1 cm. above the center of the reflector R as shown in Fig. 3. R was connected directly to earth and p to earth through the galvanometer. A second experiment was arranged as in Fig. 4. Here the plate p was parallel to

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the reflector and separated from it by an earthed brass screen *S*. The magnetic field was produced by a horseshoe magnet and of course was not at all uniform. The strength of the magnet may be estimated from the observation that when brought within 3.5 cm.

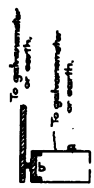

Fig. 2.

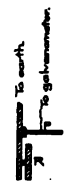

Fig. 3.

Fig. 4.

of the axis of the discharge portion of the tube the cathode rays at a potential of 4,000 volts were bent on a radius of about 4 cm. The results of the two experiments are shown in Tables IV. and V.

TABLE IV. (See Fig. 3.)

Discharge P. D. 6,500 Volts.

Distance Magnet to Reflector.	Galvanometer Deflections. 10^{-7} amp.
Negative Particles Deflected Upward.	
∞	+0.06
9.5 cm.	−0.51
6.5	.92
5.5	1.15
4.5	1.38
3.5	1.72
Negative Particles Deflected Downward.	
3.5 cm.	+0.46

TABLE V. (See Fig. 4.)

Discharge P. D. 3,000 Volts.

Distance Magnet to Reflector.	Galvanometer Deflections. 10^{-7} amp.
Negative Particles Deflected Upward.	
∞	±0
9.5 cm.	−0.05
7.5	.07
6.5	.14
5.5	.18
4.5	.28
3.5	.35
Negative Particles Deflected Downward.	
3.5	±0

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These observations show three things: (1)[1] That without magnetic field the negative emission strikes the plate *p*, Fig. 3, and hence is not confined to a direction at right angles to the reflector and is diffuse. (2) When the negative particles are deflected away from *p*, Fig. 3, the deflection of the galvanometer is positive showing that there is a slight diffuse reflection of the canal rays themselves. (3) Both tables show that even with very weak fields tending to deflect the negative particles toward the plates the negative current is increased, but even the strongest field applied is insufficient to bring the negative current to a maximum. This indicates that there are particles of widely varying velocities in the emission some extremely slow and some whose velocities can not be much less than 0.2×10^{10} cm./sec. and may be very much greater.

Regarding the mechanism of the secondary radiation it is difficult to say anything with certainty. It is clear that, as the radiation takes place in a space free from any differences of potential, all parts being connected to earth, the energy not only for the separation of the negative electrodes but also for their velocity must come from the canal rays themselves unless we are willing to assume that their impact on the metal renders its atoms radioactive so that the electrons are expelled by some process of explosion. The fact that the emission of the electrons is greater at larger angles of incidence is also difficult of explanation especially in this case when the canal rays do not penetrate the metal surface and the explanation suggested by J. J. Thomson[2] for the increased emission at large angles due to cathode rays cannot apply.

We have in the emission of negative electrons by a bombardment of positive particles a condition of things very similar to that involved in the passage of negative electricity into the gas at the cathode in the ordinary vacuum discharge, as in that case also it is generally believed that the negative particles are liberated by the impact of positive particles upon the cathode. If indeed the mechanism of the two cases is the same the present work indicates means of studying the nature of this portion of the discharge in vacuum under simplified conditions.

[1] Without magnetic field the deflections in the first experiment were sometimes positive and sometimes negative.

[2] J. J. Thomson, Conduction of Electricity through Gases, p. 509.

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Summary.

1. When canal rays strike an earthed metal surface there is a weak diffuse reflection of these rays.

2. There is also a diffuse emission of negative particles having widely varying velocities.

3. This negative emission increases as the angle of incidence of the canal rays increases and is probably similar in character to the secondary negative emission produced by cathode rays.[1]

National Bureau of Standards, Washington.

[1] Since the above was written Professor J. J. Thomson's article: Some Experiments on Kanal-Strahlen, Proc. Camb. Phil. Soc., Vol. 13, Part 4, p. 212, 1906, has appeared.

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PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

ON THE RELATIVE PROPORTION OF THE TOTAL α-RAY ACTIVITY OF RADIOACTIVE MINERALS DUE TO THE SEPARATE RADIOACTIVE CONSTITUENTS.[1]

BY B. B. BOLTWOOD.

THE maximum α-ray activity of a considerable number of radioactive minerals was measured and compared with the activity of known quantities of pure uranium, thorium and radium. The relative decrease in activity due to the removal of known quantities of radium emanation and products of rapid change from the minerals and radium salts was also determined. The activity of the polonium and actinium separated from known quantities of minerals was compared with the activity of the uranium contained in the same minerals. From the data thus secured it is possible to calculate the relative proportion of the α-ray activity of minerals due to the separate radioactive constituents. It was found that the quantity of actinium present in minerals is proportional to the uranium contained in them, which is likewise the case with polonium when the mineral does not spontaneously evolve radium emanation. The activity due to thorium was found to be proportional to the quantity of this element contained in the mineral as indicated by chemical analysis. It was observed, however, that the specific activity of the thorium obtained from certain commerical salts of thorium was only one half that of the thorium contained in, and by certain methods separated from, the natural thorium minerals.

The general conclusions reached in the paper are: (1) That actinium is a disintegration product of uranium; (2) polonium is a disintegration product of radium through the emanation; (3) that radiothorium is a disintegration product of ordinary chemical thorium, which is elementary in character, and (4) that the α-ray activity of minerals in radioactivity equilibrium is equal to the sum of two factors, one of which depends only on the amount of uranium present and the other only on the amount of thorium contained in the mineral.

[1] Abstract of a paper presented at the meeting of the Physical Society held February 24, 1906.

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Volume XXII. *June, 1906.* *Number 6.*

THE

PHYSICAL REVIEW.

MERCUROUS SULPHATE AND THE STANDARD CELLS.

By G. A. Hulett.

THE question as to the best method of preparing the mercurous sulphate and the depolarizer for standard cells does not yet seem to be satisfactorily settled. Mr. F. E. Smith [1] proposes four methods for trial: (*a*) The electrolytic method; (*b*) by adding drop by drop mercurous nitrate to a strong sulphuric acid solution; (*c*) mercurous sulphate is dissolved in strong sulphuric acid and precipitated by diluting; (*d*) by the action of fuming sulphuric acid on mercury at ordinary temperatures. Mr. Smith invites various workers to construct cells according to his specifications and forward them to the National Physical Laboratory where they may be compared. This should give interesting information as to the reliability of the various methods.

H. v. Steinwehr [2] concludes from a few experiments that the principal if not the only cause of the variation of the E.M.F. of standard cells is traceable to a difference in the size of the particles of the mercurous sulphate used as depolarizer. It is well known that a fine-grained sample of a salt has a greater solubility, and therefore its solution will show a greater E.M.F. than the solution of a coarser-grained sample of the same salt. H. v. Steinwehr concludes from theoretical considerations that variable amounts of the

[1] Electrician, 55, 856, 1905.
[2] Zeit. Instrumentk., 20, 205.

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hydrolyzed basic salt in the depolarizer could not be the cause of the variations observed in the E.M.F. of standard cells.

Last fall a number of cells were made which give experimental evidence on these important points. The main object of the work was to determine the effect of varying not only the strength of the sulphuric acid used in making the electrolytic mercurous sulphate, but the effect of varying the current density for a given strength acid. Samples of the sulphate were made by passing an electric current from a mercury anode into sulphuric acid. The concentrations of the acid used were .05 molecular, .5 molecular, molecular and 2.6, 3.7 and 12 times molecular, while the current densities were varied from 0.1 amp. to 5 amp. per 100 cm.^{2} mercury anode surface. The details of the method employed in making these various samples will be described below.

Some of the samples were gray and others white. With a low current density the white product appeared while higher current densities gave the gray. The point at which the gray appeared depended also on the strength of the acid used. With 2.6 molar acid the product was gray at a current density of 0.3 amp. and above, while with molecular acid the product was still white with 5 amp. per 100 cm.^{2} surface.

The gray preparation seems to give more uniform results than the white and a slightly lower value of the E.M.F. One is inclined to attribute this grayness to finely divided mercury, probably an "anode slime" which appears only at the higher current densities, but a high power microscope did not with certainty confirm this supposition. If the grayness is due to mercury it must be in an exceedingly fine state of division and would be an advantage as it would tend to prevent the formation of mercuric mercury.

Previous experiences have shown me that the comparison of samples in an *H* cell with a common electrolyte is often misleading, therefore the various samples were actually tested in cells in which all the other materials were the same. Further the cells were kept in a large constant temperature oil bath and compared at frequent intervals for several months. The bath contained 100 liters of kerosene oil and was electrically heated and controlled. The temperature was maintained constantly at 25° C. and has very

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seldom varied .02° from that temperature. Certificated thermometers were used to determine the temperature.

The cells were placed in wooden racks, and all the anode wires were joined together while the cathode wires passed up through little glass tubes which extended 15 cm. above the racks, ending near the top of the bath, where they were very accessible. The bath now contains 120 cells, some of them over two years old. The comparisons were made by means of a Feussner potentiometer (built by Otto Wolff, Berlin) and a sensitive D'Arsonval galvanometer. The apparatus worked very satisfactorily, a difference of 0.00001 volt caused a deflection of 2 mm. on the scale. The unit chosen for this and the previous work was the international volt, which is based on the Clark cell made according to the old specifications with an assumed value of 1.434 volts at 15° C.

The cells here considered are of the usual form and were hermetically sealed. The cadmium sulphate used was carefully recrystallized and only the perfectly clear well-rinsed crystals were used. A large stock of 12.5 per cent. cadmium amalgam was made from pure materials, and the mercury was distilled.[1] The cells were made as nearly alike as possible with the exception of the depolarizers to be tested. Precautions were taken to avoid hydrolysis in removing the acid from the various samples of mercurous sulphate, and attention was given to uniformity in making the pastes.

Table I. gives the observations made on these cells, column 1 gives the number of the cell, column 2 the date of construction, column 3 gives the strength of sulphuric acid from which the mercurous sulphate of the depolarizer was made, and column 4 gives for each case the current density employed and is expressed in amperes per 100 cm.^{2} mercury anode surface.

Attention is called to the last six cells (A21 to A25 incl.). The depolarizers of these cells were made from acid of *less* than molecular concentration and the values are higher than the others and are irregular, while all the rest of the cells made from molecular sulphuric acid or stronger than molecular, are in good agreement. There is hardly a suggestion of an effect due to dif-

[1] PHYSICAL REVIEW, 21, 388. 1905.

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TABLE I.

Cell.	Date.	Source of the Acid	Hg_2SO_4 D_{100}	Oct. 26.	Nov. 15.	Nov. 18.	Nov. 22.	Nov. 30.	Dec. 10.	Dec. 17.	Dec. 24.	Jan. 1.
A1	Oct. 21	2.7 molar	0.82 amp.	1.01905	1.01905	1.01906	1.01905	1.01905	1.01904	1.01905	1.01905	1.01905½
A2	"	"	"	04	05½	05	04½	05	05	05	05	05
A3	"	"	"	04	06	05	05½	05½	05	05½	05	05
A4	"	"	"	05	05½	05	05	06½	05½	06	05½	05½
A5	"	"	"	05	05½	05	06	05½	05	05½	05	05
A6	"	"	"	05	05	05	06	05½	05½	06	05	05
A9	Nov. 15	"	0.20 amp.			06	02½	02	03½	03	03	04
A10	"	"	1.5 "			05	03	04	04	04	04	05
A32	Dec. 15	12 molar	0.25 "								04	04
A33	"	4 molar	0.26 "								04	04½
A12	Nov. 21	1 molar	1.0 "				07	07	07	07	07	08
A13	"	"	2.5 "				06	07	06	05½	06	07
A14	"	"	5.0 "				04½	07	04	04	04½	05½
A15	"	"	0.2 "				09	11	08	08½	08½	09
A21	Nov. 27	½ molar	0.2 "					16	16	18	17½	15½
A21	"	"	1.0 "					09	08½	08	08	07
A22	"	"	4.0 "					14	15	14	15	14
A23	"	$\frac{1}{20}$ molar	0.2 "					25	22	19	20	22
A24	"	"	0.5 "					30	26	25	25½	27
A25	"	"	2.5 "					34	30	29	28	26

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TABLE I. — *Continued.*

Cell.	Date.	Source of the Acid	Hg_2SO_4 D_{100}	Jan. 6.	Jan. 13.	Jan. 20.	Feb. 1.	Feb. 7.	Feb. 20.	Mar. 4.	Mar. 15.	Mar. 31.
A1	Oct. 21	2.7 molar	0.82 amp.	1.01905	1.01905	1.01904	1.01905	1.01905	1.01905	1.01903½	1.01904	1.01905
A2	"	"	"	05	05	04½	05	05	05	03½	04	05
A3	"	"	"	05	05	04½	05	05	05	03½	04	05
A4	"	"	"	05	05	05	05½	05	05	04	04½	05
A5	"	"	"	05	05	05	05	05	05	03½	04	05
A6	"	"	"	05½	06	05	05	05½	05	04	05	06
A9	Nov. 15	"	0.20 amp.	03	03	03	04	04	03½	04	03½	05
A10	"	"	1.5 "	04½	04½	04	05	05	04½	05	05	06
A32	Dec. 15	12 molar	0.25 "	03	03	04	04	02	02½	00	02	03
A33	"	4 molar	0.25 "	04½	04	06	05	05	05	02	04	04
A12	Nov. 21	1 molar	1.0 "	07½	07½	06½	07½	07½	07½	05	07	08
A13	"	"	2.5 "	06	06	05	06½	06	06	04	06	07
A14	"	"	5.0 "	05½	05	03½	05	04½	04½	02	05	06
A15	"	"	0.2 "	08½	08½	07	08	08½	08	05	07½	08
A20	Nov. 27	½ molar	0.2 "	15	17	15	18	18	17	15	16	17
A21	"	"	1.0 "	08	10	07	08	07	07	06	07	08
A22	"	"	4.0 "	18	19	14	15	14	14	13	14	15
A23	"	$\frac{1}{10}$ molar	0.2 "	21	20	18	20	18	18	17	18	19
A24	"	"	0.5 "	23	24	23	24	23	23	22	23	24
A25	"	"	2.5 "	24	23	24	26	25	23	21	20	19½

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ferent current densities used in making the mercurous sulphate, but the strength of the acid used certainly does play a rôle as soon as it becomes less than molecular. This is also the strength acid at which the solubility curve (of mercurous sulphate in varying concentrations of sulfuric acid) shows a sharp break.[1] The solubility is .208 grams of the sulphate in a liter of 4 times molecular acid, and increases to a maximum of .550 grams in a liter of molecular acid. Here the curve takes a sharp turn downward, it is .502 gram in .5 molar and .455 gram in .25 molar and .384 gram of mercurous sulphate in a liter of .05 molar sulphuric acid, all at 25° C.

Molecular sulphuric acid then represents a point of discontinuity in the solubility curve and also for the behavior in cells of mercurous sulphate made from various concentrations of the acid. The principal conclusion to be drawn from the standpoint of standard cells is that, in making mercurous sulphate, one may use any strength of sulphuric acid from molecular to concentrated, and any desirable current density. The results obtained with these cells are very favorable for the electrolytic method of preparing the sulphate, for it must be remembered that for each cell a particular sample of paste was made, requiring separate manipulations. They are, therefore, without the advantage of cells made from one uniform batch of paste.

The question of a possible effect of the size particles on the solubility of mercurous sulphate was considered when the method was devised, and it was found that there was not a measurable effect with the electrolytic preparations. Attention was called to this in the necessary precaution of stirring the system, after the current was broken, so that the very finest particles might disappear.[2]

H. v. Steinwehr has lately[3] called attention to this point and claims for it the principle cause of the variations observed in the E.M.F. of cells. Experimental evidence on this point is contained in Table I. The mercurous sulphate used in each cell was microscopically examined and the size of the particles measured. In the case of the

[1] Hulett, Zeit. Phys. Chem., 49, 494, 1904.
[2] Hulett, Zeit. Phys. Chém., 49, 486.
[3] Zeit. Instrumentk., 25, 205. 1905.

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first fourteen cells, or all of those samples of sulphate made from molecular or stronger acid, the particles vary over a wide range, from .002 mm. to crystals .070 × .130 mm. but it will be observed that these cells are all in good agreement.

The samples made from molecular acid were uniformly larger-grained than the other samples. This was to be expected as with this strength acid the sulphate has the maximum solubility. The sample made with .2 amp. was particularly large-grained, and this sample was stirred with the acid and the finest particles decanted until only the very coarsest were left and these were taken for the depolarizer of cell A15. Now it will be seen that the E.M.F. of this cell is not lower but *higher* than the other cells. Furthermore the cells A21 to A25 which have a high value, were constructed with mercurous sulphate made from less than molecular acids, but these samples were decidedly coarser-grained than the samples used in cells A1 to A6. Since finer particles are more soluble, their solution should *increase* the E.M.F. of the cells which are made with the finer-grained depolarizers. Therefore the above results show that the effect of size of particles, in the electrolytic preparations, is not measurable and that whatever deviations there are must have some other explanation.

The microscopic observations made on the samples of electrolytic mercurous sulphate indicated that the higher current densities gave finer-grained but more uniform preparations, and also that the solubility of the sulphate had an effect in the sense that the average size of the particles are smaller in the samples made from the more concentrated acids where the solubility is less. The sample made from 2.6 molecular acid with a current density of 1.5 amp. was carefully examined and found to contain for the most part particles .004 to .008 mm. with few over .010 mm. In all the samples of electrolytic mercurous sulphate examined, comparatively few particles that measured less than .002 mm. were noticed and the failure to find variations in the E.M.F., due to size of particles, with these samples agrees with the work done on the effect of size of particles on the solubility of gypsum and barium sulphate. A measurable increase in the solubility has not been obtained until these powders contained a *large number* of particles of less than .002

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mm.[1] Commercial mercurous sulphate is very fine-grained, as has been pointed out by H. v. Steinwehr (*l. c.*), and it is well attention has been called to this question of a possible effect of the size of the particles.

THE QUESTION OF HYDROLYSIS.

The complete removal of the acid from the mercurous sulphate before making the paste is important, as sulphuric acid has a very marked effect on the E.M.F. of the cadmium cell, causing a low value. In removing the acid hydrolysis will take place if water or a too dilute acid is used in washing the sulphate. An acid salt is formed and goes into solution while a slightly soluble basic salt remains mixed with the washed salt.[2] The effect that this basic salt has on the E.M.F. of cadmium cells was tested as follows: Some electrolytic mercurous sulphate was washed with absolute alcohol and thoroughly dried. Part of this was completely hydrolyzed by treating it with successive portions of water.[3] The hydrolyzed and normal salt were then mixed in known proportions. Six samples were made containing respectively .1, .5, 1, 5 and 10 per cent. of the basic salt and these were used in cells A35 to A40 (Table II.). It was found that the effect on the E.M.F. of the cells was not constant but varied with the amount of the basic salt present in the depolarizer. The variation, while not uniform, in general increases with the amount of the basic salt.

When the normal salt is shaken with water the hydrolysis goes to the equilibrium point and stops until more water is added. By using definite amounts of salt and water a known amount of the basic salt is left with the solid. Here the effect is even greater as shown by the cells (A44 to A46). In these cells the sulphate of the depolarizer was formed by stirring normal mercurous sulphate with water and mercury until no further change took place and then the amount of the basic salt in the solid depended on the relative amounts of salt and water taken. In this way samples conatining 1, 3 and 10 per cent. of basic salt were prepared and used in

[1] Hulett, Zeit. Phys. Chem., 37, 385, 1901.
[2] Gouy, Compt. rend., 130, 1399, 1900; Hulett, Zeit. Phys. Chem., 49, 493.
[3] Gouy, l. c.

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TABLE II.

Cell.	Date.	Mercurous Sulphate.	Nov. 15.	Nov. 16.	Nov. 22.	Nov. 30.	Dec. 10.	Dec. 17.
A7	Nov. 15	Kahlbaum's mercurous sulphate.	1.02235	1.02208	1.02001	1.01947	1.01936	1.01935
A11	Nov. 19	Kahlbaum's mercurous sulphate rotated with mercury and 1.4 molar acid.				26	22	23
A29	Dec. 3	Kahlbaum's mercurous sulphate rotated with mercury and 3.7 molar acid.					15	15
A30	Dec. 15	Kahlbaum's mercurous sulphate rotated with mercury and 12.7 molar acid.						20
A26	Nov. 27	(Chemically) mercurous nitrate—sulphuric acid 90°.					22	21½
A27	"	(Chemically) mercurous nitrate—sulphuric acid 20°.					20	20½
A28	"	Mercuric sulphate reduced by mercury.					11	10½
A35	Dec. 21	0.1 per cent. basic mercurous sulphate added.						
A36	"	0.5 per cent. basic mercurous sulphate added.						
A37	"	1.0 per cent. basic mercurous sulphate added.						
A38	"	5.0 per cent. basic mercurous sulphate added.						
A39	"	10 per cent. basic mercurous sulphate added.						
A40	"	50 per cent. basic mercurous sulphate added.						
A44	Jan. 5	Mercurous sulphate stirred with 8 parts of water and mercury 1 per cent. basic.						
A45	"	Mercurous sulphate stirred with 75 parts of water and mercury 3 per cent. basic.						
A46	"	Mercurous sulphate stirred with 25 parts of water and mercury 10 per cent. basic.						

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TABLE II.—*Continued.*

Cell.	Date.	Mercurous Sulphate.	Dec. 24.	Jan. 1.	Jan. 6.	Jan. 13.	Jan. 20.	Feb. 1.
A7	Nov. 15	Kahlbaum's mercurous sulphate.	1.01935	1.01935	1.01935	1.01934½	1.01933½	1.01934½
A11	Nov. 19	Kahlbaum's mercurous sulphate rotated with mercury and 1.4 molar acid.	21½	24	23½	24½	20½	23
A29	Dec. 3	Kahlbaum's mercurous sulphate rotated with mercury and 3.7 molar acid.	18	21	17	19	20½	22
A30	Dec. 15	Kahlbaum's mercurous sulphate rotated with mercury and 12.7 molar acid.	18	20	23	21	19	21
A26	Nov. 27	(Chemically) mercurous nitrate—sulphuric acid 90°.	21½	21	22	23	29	18
A27	"	(Chemically) mercurous nitrate—sulphuric acid 20°.	19½	20	20	20	17	17
A28	"	Mercuric sulphate reduced by mercury.	12	14	12	12	10	13
A35	Dec. 21	0.1 per cent. basic mercurous sulphate added.		09	10	11	10	10
A36	"	0.5 per cent. basic mercurous sulphate added.		08	08	09	07	07
A37	"	1.0 per cent. basic mercurous sulphate added.		07	07	07	06	05
A38	"	5.0 per cent. basic mercurous sulphate added.		15	14	15	14	13
A39	"	10 per cent. basic mercurous sulphate added.		21	20	21	19	18
A40	"	50 per cent. basic mercurous sulphate added.		46	44	44	41	41
A44	Jan. 5	Mercurous sulphate stirred with 8 parts of water and mercury 1 per cent. basic.				40	35	36
A45	"	Mercurous sulphate stirred with 25 parts of water and mercury 3 per cent. basic.				27	22	24
A46	"	Mercurous sulphate stirred with 75 parts of water and mercury 10 per cent. basic.				61	56	56

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TABLE II.—*Continued.*

Cell.	Date.	Mercurous Sulphate.	Feb. 7.	Feb. 20.	Mar. 4.	Mar. 15.	Mar. 31.
A7	Nov. 15	Kahlbaum's mercurous sulphate.	1.01934	1.01933	1.01931	1.01932	1.01933
A11	Nov. 19	Kahlbaum's mercurous sulphate rotated with mercury and 1.4 molar acid.	18½	20	18	22	24
A29	Dec. 3	Kahlbaum's mercurous sulphate rotated with mercury and 3.7 molar acid.	20	19	17	19	20½
A30	Dec. 15	Kahlbaum's mercurous sulphate rotated with mercury and 12.7 molar acid.	19½	19	16	18	18
A26	Nov. 27	(Chemically) mercurous nitrate—sulphuric acid 90°.	17	20	19	20	22
A27	"	(Chemically) mercurous nitrate—sulphuric acid 20°.	15	—	—	17	18
A28	"	Mercuric sulphate reduced by mercury.	11	11	10½	12	14
A35	Dec. 21	0.1 per cent. basic mercurous sulphate added.	09	08	06	07	08
A36	"	0.5 per cent. basic mercurous sulphate added.	06	06	04	05	06
A37	"	1.0 per cent. basic mercurous sulphate added.	05	04	03	03	04
A38	"	5.0 per cent. basic mercurous sulphate added.	12	11	10	10	11
A39	"	10 per cent. basic mercurous sulphate added.	17	16	15	15	15½
A40	"	50 per cent. basic mercurous sulphate added.	39	35	35	33	33
A44	Jan. 5	Mercurous sulphate stirred with 8 parts of water and mercury 1 per cent. basic.	31	30	28	27	27
A45	"	Mercurous sulphate stirred with 25 parts of water and mercury 3 per cent. basic.	20	20	17	17	17½
A46	"	Mercurous sulphate stirred with 25 parts of water and mercury 10 per cent. basic.	49	46	42	41	41

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cells A44, A45, A46. Here the effect on the E.M.F. is very marked, and also variable.

It was to be expected that the presence of the basic salt on the depolarizer would increase the E.M.F. of the cell since the salt has a slight solubility but it is surprising that there should be such a marked variation when the per cent. of the basic salt was varied. Any mixture of the normal and basic salts such that both are in excess after the solution is saturated should yield a definite solution that is independent of the relative amounts of the two salts. H. v. Steinwehr used this argument to prove that the basic salt could not cause variations in the E.M.F. of cells. But in view of the above facts one must rather conclude that changes are taking place in this system with the possibility of new phases being formed. Further evidence that the cathode leg of the cadmium cell is not a system in equilibrium will be given in another article.

The similar behavior of the samples containing the basic salt (cells A44 to A46) and those made from less than molecular acid (cells A21 to A25) suggests that hydrolysis begins as soon as the acid becomes less than molecular. One might expect a larger amount of basic salt in the sample made from the diluter acids since hydrolysis, if it occurred, would go on until a solution was formed which would prevent further change. Hydrolysis then would be the explanation of the break in the solubility curve at molecular concentration. Further evidence for this view is that an analysis of a sample of the sulphate made from one half molar acid indicated the presence of a basic salt.[2] The behavior in cells of the samples of sulphates made from less than molecular acids makes it difficult to assume the existence of an allotropic modification as explaining the break in the solubility curve. On the other hand Cox[1] concludes from Gouy's results and some of his own observations, that there is only one basic mercurous sulphate and that the basic and normal salts are in equilibrium with .002 molecular acid. It is evident that more work needed on this question of the hydrolysis of mercurous sulphate.

The results here recorded, however, show that one cannot allow the strength of the sulphuric acid, used in making mercurous sul-

[1] Zeit. Anorg. Chem., 40, 178, 1904.
[2] Zeit. Phys. Chem., 49, 496.

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phate for standard cells, to become less than molecular. Until further evidence is at hand on the question just considered, it seems best to keep the mercurous sulphate, to be used in standard cells, from coming in contact with sulphuric acid of less than molecular concentration.

Samples of mercurous sulphate from other sources than electrolytic were also used, and the record of these cells will be found in Table II. Cell A7 was made from Kahlbaum's mercurous sulphate. The paste for this cell was washed with water and made according to the old specifications. It had a very high value at first and required about a month at 25° to reach a fairly constant value, and then it was .00030 v. higher than the cells made with electrolytic sulphate. A few experiments were made to test the effect of treating commercial mercurous sulphate with sulphuric acid and mercury. Samples of Kahlbaum's preparation were stirred twelve hours with sulphuric acid and mercury, using different concentrations of acid (from 1.4 to 12 molar). The pastes were made as described later. Cells A11, A29 and A30 are the ones here considered, and while the method of treatment yields a lower value than cell A7, it is not satisfactory. Probably a longer stirring would give a better agreement and nearer the value given by the electrolytic.

For cell A28 the mercurous sulphate was made by reducing mercuric sulphate by stirring it with mercury and sulphuric acid. The method is simple and has the advantage of producing much finely divided mercury. This cell has given satisfactory results and one similarly made two years ago[1] behaved particularly well from the first, this cell, G3, was under observation for eighteen months.

The mercurous sulphate of cells A26 and A27 was made by adding a strong solution of mercurous nitrate to sulphuric acid which was in excess and did not become less than molecular in strength. These cells are distinctly higher than the cells made with electrolytic sulphate, and higher than others I have made with "chemically" prepared sulphate, some of which were very close to the electrolytic, but never as uniform.

[1] Hulett, Zeit. Phys. Chem., 49, 488.

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The evidence given by the above-described cells and also the results of the previous work indicate that the electrolytic mercurous sulphate is the most reliable preparation, and that cells made from it are reproducible to 1 or 2 parts in 100,000. It seems well therefore to give a detailed description of the method of preparation based on the results so far obtained.

THE PREPARATION OF ELECTROLYTIC MERCUROUS SULPHATE.

The accompanying cut represents the essential parts of the apparatus needed. A battery jar some 15 cm. in diameter and 20 cm. tall is well suited to the purpose. Mercury to the depth of 2 cm. is put into the jar and is covered with sulphuric acid to a depth of

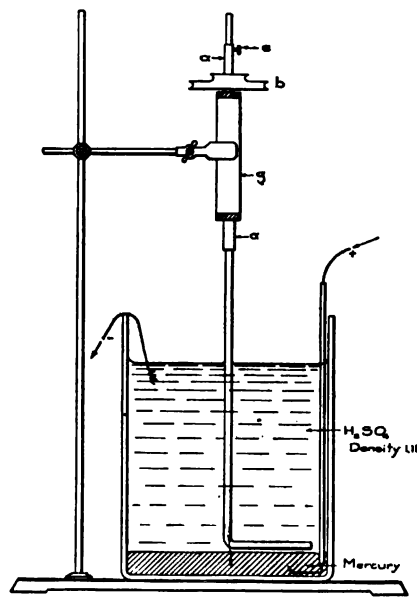

Fig. 1.

15 cm. The strength of the acid used may vary over a considerable range as has been shown. The formation of the sulphate removes an equivalent amount of acid and for several reasons it is best to use 2 or 3 times molecular. If one volume of strong sulphuric acid (1.84 density) is poured into six times its volume of

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water, the strength will be about 2.6 molecular. If the acid is made by density it should be about 1.15, and with the two liters used in the jar one may prepare several hundred grams without reducing the strength of the acid to 2 times molecular.

In order to insure contact with the mercury a stiff platinum wire (.8 mm. or over) is sealed into a glass tube with the free end 4 or 5 cm. long. This platinum wire is bent at right angles and extends well out into the mercury when the glass tube is clamped in position. The object of this is to insure contact with the mercury when the solid sulphate collects in the angle of the jar under the mercury. The copper wire from the positive pole of the battery is pushed down inside the glass tube, contact with the platinum wire is insured by running in a little mercury.

A platinum wire suspended in the acid serves as cathode. Here one needs a small surface and large current density in order that much hydrogen and relatively little mercury may be deposited. The solubility of mercurous sulphate in 2.6 molar acid is .4 gram per liter, and with the above arrangement the yield is very good, about 9 grams per ampere-hour.

A motor-driven stirrer is necessary and it is important that the bearings work smoothly. The sketch represents a very simple arrangement. A brass tube (*a*) 8 mm. in diameter is provided with a pulley wheel (*b*). This tube holds the glass stirrer which is made fast by the set screw (*e*), the brass tube turns in the iron bearings which are soldered into the ends of a larger 15 mm. diameter brass tube (*g*). This outer-bearing tube may be clamped in any ordinary clamp. A glass rod that fits the inner brass tube is selected and clamped in the tube. The glass rod extends about 40 cm. below the holder and is bent at right angles. The stirrer is adjusted to the jar so that the *L* part of the stirrer just escapes the mercury when rotating at a rate of about 200 revolutions per minute. Some experience is necessary to adjust the stirrer properly, if the mercury is unduly disturbed much of it will become finely divided and be troublesome.

After all is in order and the stirrer working smoothly, the current is turned on and as soon as the acid is saturated the solid sulphate will appear on the surface of the mercury and form a skin which

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does not always break up at once. This difficulty, which happens only when fresh acid and mercury are used, may be avoided by making and breaking the current several times until the solid appears throughout the acid after which no further trouble will be experienced. A current of 2 or 3 amperes may be used and will form some 25 grams an hour. The rapid stirring will keep the mercury surface sufficiently free of the solid until some 50 grams have formed, if more is needed it is best to remove the sulphate and start again, using the same acid and mercury but not allowing the acid to get much below 1.15 in density.

When sufficient mercurous sulphate has formed, the current is broken and the motor stopped. After the solids have settled most of the liquid is decanted (some of it in a wash bottle for assisting in the operations of transferring the solids). The solids and mercury are transferred to a large separatory funnel and the mercury removed. The sulphate finely-divided mercury and about a liter of the liquid are returned to the jar, or run into a large Erlenmeyer flask, and stirred over night. The object of this stirring is to allow the sulphate to become coarse-grained and unless most of the mercury is first removed the sulphate will often collect under it and the action is retarded. After twelve hours' stirring the sulphate settles rapidly and leaves the liquid perfectly clear. The product is still quite gray and is to be kept under the acid from which it was made and protected from the light. It is well to take precautions to protect the sulphate from the light during all the operations.[1]

PREPARING THE PASTE.

The results here recorded show that the basic salt, formed by treating mercurous sulphate with water or too dilute acid, effects the E.M.F. of the cell when it is present in the depolarizer. A

[1] The effect of light is to turn the sulphate brown and then black. Just what change takes place does not seem to be known. Two years ago a cell was made up with this blackened sulphate and had a value of 1.02038 (25°) to start with and decreased all the time it was observed (four months). At the same time some cells were made and half of them were protected from the light, by covering with asphalt paint and shellac, but in a year's time there was no distinct difference between the cells. The brown seems to form only on the surface next to the glass and it seems probable that with ordinary usage there is no effect after the cell is made, but the mercurous sulphate should not be exposed to strong light before it is put into the cell.

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higher value is obtained than when the normal salt alone is used, and the effect varies irregularly with the amount of this basic salt present in the deplorarizer. Until this anomaly is cleared up it seems best to avoid the basic salt all together.

The old method of washing the salt with water gave quite uniform results when the cells were made from a particular sample of sulphate, and with a uniform preparation like the electrolytic mercurous sulphate, the old method of washing might do very well. One point is however to be considered, if water is passed through the sulphate in a filter the top layer only turns yellow, evidently the water becomes saturated with the soluble products of hydrolysis and is no longer capable of effecting the lower layer.[1] This top layer has always been rejected and thus the part taken may have contained very little basic sulphate, but the liquid which could not be entirely removed is distinctly acid.[2] Last year a cadmium cell was made in which the solution was .2 molecular sulphuric acid saturated with cadimum sulphate. This cell has always been low, and has now a value of 1.01845 (25°). Acid seems to have more effect than other impurities and is to be avoided. Jaeger & Wachsmuth.[3]

The problem then is to completely remove the acid and to avoid hydrolyzing the salt. This may be done by washing with alcohol, and then once or twice with cadmium sulphate or zinc sulphate solution, as the case may be. For half a dozen cells, or less, one may use a Gooch crucible and Bunsen filtering flask. A little filter is cut from filter-paper with a large cork borer, and fitted to the crucible. The sulphate is brought into the crucible and the acid removed as completely as possible by suction, then some absolute alcohol is run in so as to wash the sides of the crucible and then drawn through the sulphate by suction. This is repeated five or six times, using only a few c.c. of alcohol each time. The alcohol is removed by washing once or twice with a saturated solution of cadmium or zinc sulphate as the case may be.

The washing with alcohol is much more rapid and in general more effective than with the rather viscous sulphate solutions. If

[1] Zeit. Phys. Chem., 49, 497.
[2] L. c., 497.
[3] Wied. Ann., 59, 586, 1896.

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the sulphate is washed only with the alcohol and the paste made without completely removing the alcohol the results are good, but it is best to finally wash once with the saturated sulphate solution to be used in making the paste. In washing larger amounts one may use a small Buchener funnel and filtering flask. For thorough washing it is best not to have the sulphate over 2 cm. deep.

The washed sulphate is mixed with about one fourth its volume of finely-powdered cadmium sulphate or zinc sulphate as the case may be and then the saturated solution is added with stirring until a homogeneous paste is formed. The paste should be of such a consistency that it will just flow from a tube 5 mm. in diameter. The paste may be drawn up into such a tube by slight suction and then easily and neatly introduced into the cell. The addition of mercury is not necessary with the gray electrolytic mercurous sulphate.

In the case of the cadmium cell the paste should be over one centimeter deep in the leg of the cell. A number of cells have been made with less than a centimeter of paste, some only a few mm., and they were very irregular and are now very low. The question of the changes in the cathode leg of the cadmium cell, after it is constructed, will be reported on in a succeeding article.

Dr. M. A. Hunter assisted in constructing the cells and in making the comparisons described in this article, and I take this opportunity to thank him for very valuable aid.

PRINCETON UNIVERSITY,
March, 1906.

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IMPROVEMENTS IN THE DIFFRACTION PROCESS OF COLOR PHOTOGRAPHY.

By Herbert E. Ives.

THE diffraction process of color photography, invented by Professor R. W. Wood, was first described in the *Philosophical Magazine* for April, 1899. An application of the "three-color" method of reproducing colors by photography, its distinguishing feature is the elimination of pigments as a means of producing the three primary colors, red, green, and blue, and the use, in their place, of diffraction gratings.

The production of color by the grating is utilized in the following manner: A bright point or line of light is focussed on a screen by a convex lens, over which is placed a diffraction grating. Viewed from a point in one of the resulting spectra the lens appears uniformly illuminated in the color of light incident on the eye. By choosing gratings of different spacings any desired color may be obtained at any chosen point. Consequently if the three-color positives are made in the form of diffraction gratings of three different spacings, such that one sends red, the second green, and the third blue light to the same point, the eye placed at that point will see each picture in its appropriate color, and a color picture will result from the summation of the effects of the three.

To produce diffraction color photographs Professor Wood used the bichromated gelatine process. On a glass surface so sensitized three prints were made, one over the other, from the three-color positives, each positive being placed over a glass diffraction grating of suitable spacing in contact with the gelatine surface. From the pictures obtained in this way copies could be made in turn by contact printing on other bichromated gelatine plates.

Although a process of great theoretical interest and of apparent simplicity, during the last six years all attempts to secure satisfac-

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tory pictures by the procedure outlined resulted in practical failure. The few pictures obtained were extremely interesting, as some color effects were reproduced with surprising fidelity. Far from being a simple and exact method of reproducing colors, however, the diffraction process proved in practice disappointing. It was difficult to work and quite unreliable, certain color effects were reproduced only occasionally or not at all, while an identical procedure would produce quite different results with different subjects.

Through the courtesy of Professor Wood the writer was last summer furnished with a number of diffraction gratings ruled on the Rowland engines at Johns Hopkins University. With these experiments were made in diffraction color photography, certain defects were discovered in the previous mode of working, means were found for obviating these defects, and the process thereby made to yield results of a hitherto unattainable beauty and perfection.

The fundamental defect in the original mode of making diffraction pictures was found to lie in the means for obtaining the united action of the three gratings, namely, by superposition. In order for the process to be successful each grating should act independently after superposition on the others. As a matter of fact, disturbing effects are introduced by the action of the gratings on one another. In the first place, superposition of two gratings results in a new grating of a coarser spacing whenever any simple relation exists between the two spacings. For instance, when two gratings are ruled on the same dividing engine by a change in the number of teeth "feed," regularly recurring coincidences are found on superposition, these constituting the new grating. In the second place, even when there is no simple relation between the spacings of two gratings, one acts on the other to form "ghosts" or spectra of spectra. In diffraction picture work the first effect causes light to be subtracted from the spectra used and deviated into new unused ones. Hence two colors will not add to produce a color of double luminosity. This was exhibited by the production of dirty yellows and other mixed colors. The second effect, besides occasioning loss of light, causes false color, as the "ghosts" fall in such positions that the eye receives from them different colors than from the original gratings. This case occurred frequently in practice, red

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and blue discs combining to form green instead of purple, and pink roses reproducing as green.[1]

The conclusion from these observations was that the grating effects must be added by some means other than superposition. This means was suggested by the Joly process, in which the mixture of the three colors is accomplished by breaking up the picture into narrow juxtaposed lines, alternating red, green and blue, the eye blending the three. Some experiments had previously been made by Professor Wood with Joly pictures, with the object of demonstrating the possibility of making the color lines much finer, by using strips of grating, than is possible by using pigments. For this purpose he ruled a special grating consisting of several lines of one spacing, followed by several of a second and several of a third, repeating across the plate, the width of the strips corresponding to that of original Joly pictures. By printing through this grating from the special line pictures, diffraction Joly pictures were obtained. This procedure was however open to the great disadvantage, apart from the necessity for the specially ruled grating, of dependence upon the specially made Joly originals, of a coarse spacing of lines determined by the limitations of the taking process. A much more serious objection, however, was found by the writer, namely that the lines of the picture, since they ran parallel to the diffraction grating lines, could not be made fine enough to be invisible without themselves forming a diffraction grating, throwing its spectra on those from the three principal gratings and degrading the colors.

The problem was thus reduced to finding some simple and convenient means of breaking up the picture into narrow strips of diffraction grating, and at the same time eliminating the grating effect of these strips. This was achieved by the following procedure:

In Fig. 1, which represents the method of making the improved diffraction pictures, *A* is the bichromated gelatine plate, rigidly fixed

[1] These secondary spectra were mentioned as being "rarely troublesome" by Professor Wood in Nature, October 20, 1904. In the writer's experience the conditions necessary for the best photographic copying of gratings are precisely those to give strong "ghosts."

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in position; *B* is a glass diffraction grating; *C* is a screen ruled with at least two hundred opaque lines to the inch, the opaque lines being twice the width of the transparent spaces between; *D* a lens, and *E* a three-color positive. The latter is one of a set of ordinary three-color positives, containing no lines, and the grating is an ordinary continuously ruled one, also from a set of three, each of which is calculated to send one of the primary colors to a given point, say 2,400 lines to the inch for the red, 3,000 for the green, 3,600 for the blue. With say the "red" positive at *E* and the corresponding grating at *B*, an exposure is made, resulting in a series of narrow exposed strips on which the grating structure is impressed. A second positive is then placed at *E*, the corresponding grating at *B*, and the ruling *C* is moved the width of a transparent portion. A second exposure is made, the first exposure being shielded by the opaque lines of the screen, and then a similar treatment given to the third positive. On development a picture is obtained made up of alternating strips of three different grating spacings.

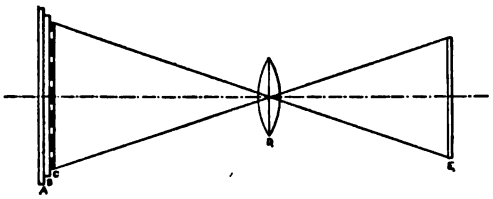

Fig. 1.

To eliminate the grating effect of the narrow strips of grating or Joly lines the latter are made to run at right angles to the diffraction grating lines so that the spectra produced by them are diverted in another direction and do not enter the eye.

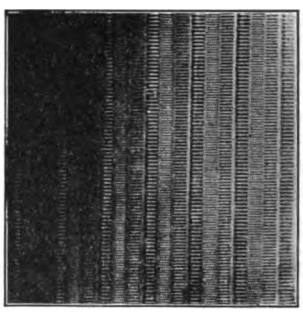

Fig. 2.

Fig. 2 is from a photo-micrograph of a portion of the finished picture. The short fine lines are the diffraction grating lines producing the three primary colors, 2,400 to the inch for the red, 3,000 for the green, 3,600 for the blue. The broad strips at right angles to the diffraction lines constitute the Joly lines, of which there

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are 200 groups of three to the inch. From these pictures, it is important to note, an unlimited number of copies can be made by simple contact printing on bicromated gelatine.

As a further modification of the original method the writer has found it possible to obtain the color effects with a single grating spacing. To do this the source of light must be a rather long slit. Viewed through a grating the slit of course gives long spectra. If now the grating be rotated about the perpendicular joining it with the slit the spectra move in toward the latter. By suitable rotation any desired color may be obtained at any given point. With a grating of 3,600 lines to the inch to give the blue when parallel to the slit, a rotation of 21½° will give the green, of 42° the red. In the absence of suitable dividing engines to rule three properly proportioned gratings this affords an exact and easy method of securing the three colors. It has the further advantage that in printing copies any defect in printing contact will affect all three colors alike, which is not the case with gratings of different degrees of fineness. Pictures made with but one grating can of course be broken up into strips precisely as those from three gratings.[1]

With these improvements probably the last word has been said on the pictures themselves. An important improvement in the means for observing them, due to the writer's father, Mr. Frederic E. Ives, must be described.

The lens and distant source of light, as used by Professor Wood, is not a convenient arrangement, nor is it desirable to use artificial light. A convenient apparatus, easily set up, not liable to get out of order, and suitable for daylight, became a necessity upon the development of the picture-making process. The instrument about to be described admirably fulfils this purpose.

The chief difficulty attending the use of daylight for diffraction pictures is lack of light. The light diverted into one spectrum by a grating is at best only a small fraction of the total, and if the

[1] Since working out the above plan the writer has learned that Mr. Thorp, of Manchester, proposed the use of a single grating some years ago. Mr. Thorp's method, however, was to use three sources of light, turning the gratings till they found their own sources and cleared the others, then moving the sources till the desired color was obtained. He found an inclination of ten degrees convenient. The idea of using a definite rotation, calculated from the wave-length of the desired color is, it is believed, new.

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sky is used as source this small fraction is not enough to be satisfactory. This difficulty has been overcome by the novel device of a series of slits, each furnishing one spectrum. In this way with four slits, two first and two second order spectra are utilized, giving at least three times the light obtainable from one slit. The use of second order as well as first order spectra, it may be noted, is a distinct advantage, in that, as gratings never give a perfectly uniform distribution of light and color, certain desirable qualities of the picture are often found in one order and not in the other, and the best possible results follow from blending the two.

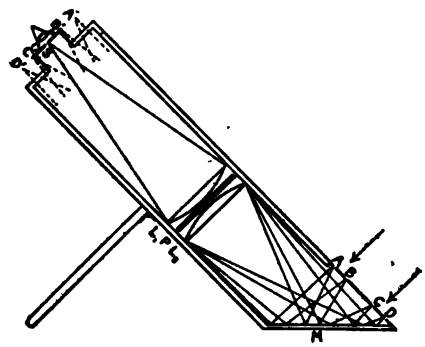

Fig. 3.

Fig. 3 gives the instrument in section, its size being about fifteen inches by three by three. A, B, C, D are the four slits; M a mirror; L_1 and L_2 lenses; P the diffraction picture (a two and a half inch circle); and S the slit through which the picture is observed. The direct images of the slits are formed at A', B', C', D'; from each of these light is diffracted to S; from B and C the first order spectra, from A and D the second order. The instrument can be made either monocular or binocular — the latter form being made possible by a horizontal disposition of the grating lines and slits.

Pictures made in the manner described are entirely free from the defects found in those previously made. Viewed in this instrument they fairly rival the results obtained in the Krōmskōp.

In conclusion the writer wishes to express his thanks to Professor Wood, not only for the original loan of gratings, but for suggestions and assistance in the past winter, during which new gratings have been ruled and much detail work done in perfecting the process. He is also greatly indebted to Mr. Max Levy, of Philadelphia, on whose ruling machines the special opaque line screens have been ruled.

PHYSICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY.

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ON THE MEASUREMENT OF THE INDEX OF REFRACTION BY THE INTERFEROMETER.

By John C. Shedd and Philip Fitch.

ONE of the simpler applications of the interferometer is that in which the instrument is used for the measurement of the index of refraction. The method, as heretofore presented, is illustrated in Fig. 1, where M is the mirror of the interferometer which is mounted on the movable carriage, and N the thin lamina whose index is to be determined. If M be first adjusted for color fringes then the introduction of N will increase the optical path by the the amount $e(\mu - 1)$ where e is the thickness of the lamina N.

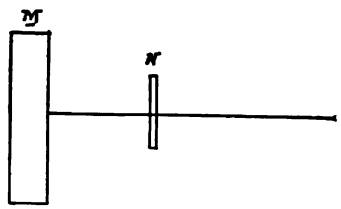

Fig. 1.

This increase in path may be measured by counting the number of fringes passed over in restoring the color fringes to the field as seen through N. If n be this number and λ the wave-length of the light used, then,

$$e(\mu - 1) = n\lambda$$

and

$$\mu = 1 + \frac{n\lambda}{e}. \qquad (1)$$

Generally, but not necessarily, the light passes through N twice and the above equation becomes,

$$\mu = 1 + \frac{n\lambda}{2e}. \qquad (2)$$

The value of n in this case is, of course, twice as great as in equation 1.

The operation of this method may be more fully outlined as follows: *First*, the thickness of the lamina N is carefully measured by

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means of a micrometer-screw or optical lever. *Second*, the interferometer is adjusted for color fringes and the lamina is placed in the path of the rays passing to and from the mirror M (Fig. 1) in such a manner as to cut them orthogonally. The mirror M is now advanced until the color fringes appear in the field as seen through N. During the movement of the mirror the number of fringes passed over is counted and the index determined from the data thus secured.

If v = the velocity of light in air,
v' = the velocity of light in the lamina N,
λ = the wave-length in air of the light used (*e. g.*, Na light),
μ = the index of refraction of N,
e = the thickness of N,
n = the number of fringes passed over.

Then $v't = e$, also $vt = e + n\lambda$.

But

$$\frac{vt}{v't} = \frac{v}{v'} = \mu,$$

and hence

$$\mu = \frac{e + n\lambda}{e} = 1 + \frac{n\lambda}{e}. \qquad (1)$$

If the light pass through N twice, then,

$$\mu = 1 + \frac{n\lambda}{2e}. \qquad (2)$$

The objection to this method lies in the fact that e must be determined by some mechanical device. If the micrometer screw be used there is the liability of compressing the lamina in making the measurement. If on the other hand the optical lever be used a lamina of considerable size and uniformity in thickness must be used. The degree of accuracy of either method of getting e is of course far less than in measuring the retardation by counting fringes.

In the present modification of the old method it is proposed to measure e by means of the same light waves which are used for getting the retardation. The same degree of accuracy is thus had in the determination of all of the terms entering into the final equation.

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To accomplish this it is necessary that the lamina be of uniform thickness and that a part of its surface be silvered. The thickness of the silver film is not important, as it is measured and allowed for. To secure uniformity of thickness the lamina is introduced into the path of the interferometer, as shown in Fig. 1. Any inequality in thickness or any strain of any sort is shown by a distortion in the fringes. It is thus very easy to select a lamina of uniform optical structure. Having secured such a lamina it is silvered in the ordinary manner, the silvering being then removed from all of one side and half of the other. It is now pressed against the mirror *M* as shown in Fig. 2. A gentle pressure is sufficient to make the lamina adhere to the surface of the mirror. Care must be exercised to apply this pressure to the center of the silvered surface *S*, so that close contact shall be made at this point. In practice it has been found that the fringes, whether chromatic or otherwise, seen from this silvered surface are always circles. This would indicate that the small surface of the lamina is in the form of a concave mirror of very slight curvature.[1]

Having the lamina in place there are now three surfaces on which fringes are to be observed, first, from the surface of the mirror *M* (see Fig. 2) outside of the lamina; second, from the surface *M*

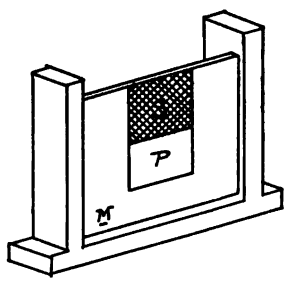

Fig. 2.

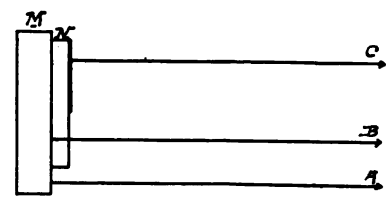

Fig. 3.

through the lamina (*P*, Fig. 2); third, from the silvered surface of the lamina (*S*, Fig. 2).

The readings to be taken are as follows: *First*, the chromatic fringers are secured on the mirror *M*. This will be the position of the ray *A*, Fig. 3. *Second*, the chromatic fringes are secured from

[1] For circular chromatic fringes see PHYS. REV., Vol. XI., page 310.

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the surface of the silver film S. This is the ray C in Fig. 3. The number of fringes counted in passing from M to S is a measure of the thickness of the lamina plus the silver film. *Third*, the count is taken back to M, and lastly the number of fringes is counted until the chromatic fringes are seen coming from M through the lamina. This count gives the retardation due to the lamina.

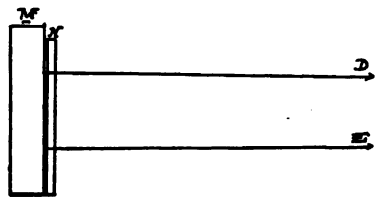

Fig. 4.

The lamina is now removed and replaced with the silvered side next the mirror as shown in Fig. 4. If now the adjustment be made so as to give the chromatic fringes from the mirror M through the lamina, and the count be taken from this position (ray D, Fig. 4) until the fringes appear from the silver film (ray E, Fig. 4) the number of fringes passed over gives the thickness of the silver film.

Let:

n_1 = the number of fringes counted in passing from A to C, in Fig. 3.

n_2 = the number of fringes counted in passing from A to B, in Fig. 3.

n_3 = the number of fringes counted in passing from D to E, in Fig. 4.

λ = the wave-length of the light used for getting the fringes.

Then we will have:

$n_1\lambda$ = twice the thickness of the lamina and the silver film,

or

$$n_1\lambda = 2(e + e').$$

Also:

$n_2\lambda$ = the retardation due to the lamina,

or

$$n_2\lambda = 2e(\mu - 1).$$

Also:

$n_3\lambda$ = twice the thickness of the silver film alone,

or

$$n_3\lambda = 2e'.$$

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Therefore

$$(n_1 - n_3)\lambda = \text{twice the thickness of the lamina alone,}$$

or

$$(n_1 - n_3)\lambda = 2e.$$

Finally,

$$n_2\lambda = 2e(\mu - 1) = (n_1 - n_3)\lambda(\mu - 1),$$

or

$$n_2 = (n_1 - n_3)(\mu - 1).$$

So that:

$$\mu = 1 + \frac{n_2}{n_1 - n_3} \qquad (3)$$

It is seen that in equation 3 all of the terms are gotten by counting fringes, and are not dependent upon any mechanical devise whatever.

In the practical working of the method the following suggestions will be found useful:

I. It will be found convenient to have cross wires placed on the lens which is used for giving parallel light to the interferometer. The images of these cross wires serve as an index in counting the fringes. The intersection of the wires should cut the center of the circular fringes.

II. After the lamina has been placed against the movable mirror it generally happens that the stationary mirror of the interferometer must be readjusted in order to secure the fringes. In making this adjustment three sets of fringes should be simultaneously present, those from the silvered surface of the lamina, those seen through the lamina and those from the free surface of the mirror. This can best be done by first securing the circular fringes from the silvered surface of the lamina and then shifting these about until the others appear.

III. The thickness of the lamina tested by the writers did not exceed .2 mm. The accuracy of the method rather increases with the thickness of the lamina used, though the counting is thereby made more tedious. The thickness of the lamina tested measured a little greater when measured by wave-lengths than when measured by the micrometer. This is to be expected when it is considered that the latter method involves a pressure on the lamina.

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The following experimental data will illustrate the results to be obtained by this method. The source of light used was the Na flame.

	n_1	n_2	n_3	μ
Glass.	598	306	11	1.521
	601	307	11	1.520
	601	308	11	1.522
Mica.	379	224	9	1.605
	380	224	9	1.603
	380	223	9	1.601
	382	224	9	1.600
	380	224	9	1.603

PHYSICAL LABORATORY,
COLORADO COLLEGE, March 5, 1906.

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CONCERNING THE TEMPERATURE OF THE NERNST LAMP.

By Leon W. Hartman.

THE early determinations of the temperature of the incandescent glower of the Nernst lamp gave values which were undoubtedly much too high. These determinations were based on the law of the radiation from a black body. To this class of radiators, however, the Nernst glower does not belong; so that if the glower emits selective radiation as compared with the radiation from a black body, its measured black body temperature might be much above its actual temperature. This is the case; hence the higher values of its temperature, as found by the early investigators, is explained.

If one avails himself of existing data and methods and applies the data and curves of Ångström [1] to the data of the writer,[2] published in a former number of this journal, a value of the temperature much lower than that cited by Lummer and Pringsheim [3] will be obtained. This discrepancy then makes a determination of the temperature of the incandescent glower by direct measurement very desirable.

When the data for the energy losses from incandescent platinum wires in air had been obtained,[4] an effort was made by the writer to utilize the same method for determining the temperature of the incandescent glower of the Nernst lamp. Briefly stated, this method was as follows: The candle power per unit length for varying power supply was first determined with a number of Nernst glowers. In front of an iridium furnace containing a piece of magnesium oxide, was then mounted a frame for the glowers, in series with which was a suitable regulating rheostat. When the furnace was heated, the magnesium within was heated up to incandescence.

[1] Ångström, Phys. Rev., 17, p. 302, 1903.
[2] Hartman, Phys. Rev., 17, p. 65, 1903.
[3] Lummer and Pringsheim, Verhd. d. Deutsch. Ges., 3, p. 36, 1901.
[4] Hartman, Phys. Zeitschr. 5, p. 579, 1904.

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Each glower in turn was then mounted on the frame and heated by a current until its color, as seen against the magnesium oxide as a background, seemed as near the color of the latter as it was possible to get it. Noting the power supply, the candle power per centimeter length could be determined from the plotted curves of the first set of observations. As soon as the power supplied was determined, the temperature of the interior of the furnace, *i. e.*, the temperature of the magnesium oxide was measured by means of a Wanner pyrometer. Some of the data thus obtained are given in the upper part of the following table.

TABLE I.

Measured Energy Supplied.

No.	Amp.	Volts.	Watts.	Watts / cm.	Tempr. (abs.)	Watts / cm.	C. P.	C. P. / mm.²
I.	0.148	173	25.6	16.3	2,360°	1.79	14.8	3.25
II.	0.410	182	74.6	36.1	2,360	1.83	42.0	3.29
III.	0.846	175	148.0	52.9	2,360	1.75	86.8	3.22
IV.	0.810	103	83.5	59.6	1,800	1.90	47.0	3.36

In obtaining these data the writer had the coöperation and assistance of Professor Nernst and one of his assistants, but at that time some doubt arose as to the accuracy of the temperature determinations thus made, and they have not been published hitherto. The writer has since decided to make some independent temperature measurements following an entirely different method, the details of which are given below.

When Professor E. L. Nichols made his observations for the determination of the temperature of the acetylene flame,[1] it was the writer's privilege to assist in a small way. It seemed probable, therefore, that the same method used in those former measurements might be used to good advantage in determining the actual temperature of the incandescent glower when the latter was carrying a given constant load. Three specimens of the same platinum and platinum-rhodium wire used in the determinations just mentioned were therefore taken, pulled down to suitable size, and made into thermo-elements. After a 110-volt glower with its ballast had been mounted on a suitable frame and connected in series with an ad-

[1] Nichols, PHYS. REV., 10, p. 234, 1900.

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justable rheostat, a current of 0.80 amperes — its rated normal load — was passed through the glower. The junction of the thermo-element was then moved slowly up to the incandescent glower. To the writer's surprise the junction could be brought in contact with the glower without melting or being otherwise visibly changed. This was true of the smallest junction used — the radius of which was 0.00360 cm. The only conclusion to be drawn was that the temperature of the incandescent glower was much lower than the early measurements indicated. The radii of the three junctions used were as follows: No. I., had a radius of 0.00592 cm.; No. II., of 0.00493 cm.; No. III., of 0.00360 cm.

The thermo-electromotive forces generated in these three thermo-elements were then measured on the potentiometer — the junction of the thermo-element being meantime in contact with the glower. From a curve, plotted from the values given by Kohlrausch,[1] the temperature corresponding to each electromotive force was then read and a curve was plotted with corresponding temperatures as ordinates and cross-sections of the wires as abscissæ. In order to eliminate conduction, this curve was extended back until it intersected the axis of ordinates. Thus one eliminated the conduction of the thermo-elements, and obtained at the intersection of the curve with the axis of ordinates, the value of the temperature that would be measured with a wire of zero cross-section. The values obtained from a series of measurements on a half dozen different glowers gave results varying from 1780° to 1800° absolute as is shown by the following table:

TABLE II.

Temperatures of Various Glowers as Measured with the Three Thermo-elements.

Glower.	Temperatures for Elements.			Exterpolated Value.
	No. I.	No. II.	No. III.	
I.	1,223°	1,407°	1,487°	1,505° C.
II.	1,220	1,430	1,500	1,515
III.	1,270	1,425	1,520	1,530
IV.	1,230	1,385	1,495	1,535
V.	1,145	1,320	1,460	1,510
VI.	1,150	1,330 (?)	1,480	1,515
			Mean value,	1,791 absolute.

[1] Kohlrausch, Praktische Physik, p. 157, 1901, 9te Aufl.

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In some cases the glower was heated by direct current; in others, by alternating current. Sometimes the glower was in the plane formed by the two wires of the thermo-junction; sometimes the glower was at right angles to the plane including the two wires. In all cases the glower was horizontal. The mean of all these measurements gives a temperature of 1791° absolute.

After making these measurements, in order to make sure that the character of the wires of the thermo-elements had not been changed by contact with the hot oxides constituting the glower, the junctions were used to measure the temperature of various parts of the luminous cone of the Bunsen flame. Values concordant with those obtained by Waggoner[1] were obtained. Although under a microscope the wires did not present a perfectly smooth appearance like that of a newly drawn wire, yet the tests to which the junctions were subjected made it seem probable that the thermo-junctions used measured the true temperature of the Bunsen flame and of the glowers as accurately as one could expect, considering that there was more or less unavoidable change in the value of the current passing through the glower.

TABLE III. (*Computed.*)

Watts per Centimeter Length Required by Black Bodies for the Absolute Temperatures Indicated Below.

No.	Thickness.	1700°	1800°	1900°	2000°	2100°	2200°
		Watts per Centimeter.					
I.	0.0290 cm.	4.10	5.11	6.35	7.81	9.50	11.44
II.	0.0618 "	8.67	10.91	13.54	16.62	20.20	24.33
III.	0.0964 "	13.50	17.00	21.10	26.87	31.50	37.90
IV.	0.1000 "	14.10	17.60	22.00	27.00	32.70	

Some comparisons will now prove of interest. It will be instructive to compare the actual energy supplied to the glower when it is heated to a given temperature, with the energy required to produce the same temperature in a black body of the same dimensions as the Nernst glower. The computed data for the black body are given in Table III. For the absolute temperatures indicated in this table,

[1] Waggoner, Wied. Ann., 58, 579, 1896.

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the energy per centimeter length required by a black body of the same cross-section as the Nernst glower is given. In Table I. data showing the energy supplied to four different glowers are given. The first three are German glowers and the accompanying data were obtained by the method first mentioned above, using the Wanner Pyrometer and the iridium furnace to determine the temperature of the glower. The last case, glower No. IV., is one of the American glowers in which case the temperature of the glower was measured by means of the thermo-element. Glowers Nos. III. and IV. of this table are so similar that a comparison is possible. For example, the current strength in the two cases, the watts per centimeter length, the energy per sq. mm., and the candle power per sq. mm., are all of such a relative magnitude as to be comparable. In case of glower No. III., whose temperature was determined by the pyrometer, the temperature was found to be 2300° absolute. Judging from the candle power per sq. mm., glower No. IV. should be considerably hotter than glower No. III., but with the glower first mentioned the thermo-element showed a temperature of 1800° absolute. Evidently, therefore, the method used to measure the temperature of No. III. gave values much too high. In other words the laws of Wien and Paschen do not apply to the Nernst glower because it is not a black body, but on the contrary shows selective radiation when compared with the radiation from the latter. These laws cannot be used, therefore, with the constants now available for a black body, in order to determine the temperature of the Nernst glower.

If now we compute the energy lost by glowers Nos. I., II. and III., assuming for the time being that the black body law is followed and that the temperature obtained from measurements based on that law are correct, we find the watts lost per centimeter length to be relatively very small, as is shown by the first part of Table IV. and the percentage loss to be very small, ranging from 5 per cent. to 7 per cent. On the other hand, if we take the temperature obtained by the thermo-element method as the correct temperature of the glower, and then find the energy required to heat a black body of the same dimensions as the glower to the absolute temperature of 1800° we find a relative large loss, viz., 42 watts, or a percentage loss at 1800° absolute of 70.5 per cent.

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The advantage from a commercial standpoint of rating the temperature of the Nernst glower above its actual value, is shown very clearly by these figures. From these considerations, it seems quite evident that the economic superiority of the glower over that of a black body is not so great as has been claimed for it. That it is far from being a black body, as has long been known, is also strikingly emphasized. That its true temperature has been placed too high is conclusive. Temperature measurements on the glower based on its radiating power or its photometric qualities, are alike apt to give values which are much too high.

TABLE IV.

Watts per Centimeter Length lost into the Air due to Conduction, Convection, etc.

No.	Absolute Temps.	Watts Lost.	Per Cent. Watts Lost.
I.	2,360°	1.01	6.2
II.	2,360	4.79	7.6
III.	2,360	2.61	5.2
IV.	1,800	42.00	70.5

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PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE THIRTY-SECOND MEETING.

A REGULAR meeting of the Physical Society was held at Washington, D. C., on Friday, April 20, and Saturday, April 21, 1906. President Barus presided.

The Friday session was held at the Cosmos Club, and the Saturday sessions at the National Bureau of standards.

The program was as follows:

FRIDAY, APRIL 20.

1. Measurements of the Internal Temperatures of Common Materials. C. B. THWING.

2. On the Influence of Frequency upon the Self-inductance of Cylindrical Coils of Any Number of Layers. (Read by title.) J. G. COFFIN.

3. On the Geometric Mean Distance of Square Areas and their Use in the Calculation of Inductances. E. B. ROSA.

4. Cheltenham Magnetic Observatory Registration of Effects from Electric Cars over 12 Miles Distant. L. A. BAUER.

5. Mica Condensers as Standards of Capacity. E. B. ROSA and F. W. GROVER.

6. The Electrolytic Wave Detector. L. W. AUSTIN.

7. On the Determination of Melting Points by Radiation Methods. C. W. WAIDNER and G. K. BURGESS.

8. Talbot's Law as Applied to the Rotating Sectored Disk. E. P. HYDE.

9. A New Potentiometer. H. B. BROOKS.

SATURDAY, APRIL 21.

10. Direct Reading Methods for Resistance Comparisons. F. A. WOLFF.

11. The Velocity and Ratio e/m for the Primary and Secondary Rays of Radium. S. J. ALLEN.

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12. New "Reststrahlen." A. H. PFUND.
13. Study of Polarization Phenomena in the Infra-red. A. H. PFUND.
14. Note on a New Form of Radiometer. W. W. COBLENTZ.
15. Fish eye Views. R. W. WOOD.
16. Interference Colors of Chlorate of Potash Laminæ. R. W. WOOD.
17. Fluorescence and Magnetic Rotation of Vapors. R. W. WOOD.
18. Resonance Radiation of Fluorescence of Sodium Vapor. R. W. WOOD.

SATURDAY AFTERNOON.

Professor H. A. Lorentz, of Leyden, addressed the Society on the subject of "Gibbs' Statistical Mechanics."

The regular program was then continued as follows:

19. The Ratio of the Electromagnetic and Electrostatic Units. E. B. ROSA and N. E. DORSEY.
20. Spectral Lines as Light Sources in Polariscopic Measurements. F. J. BATES.
21. Water of Crystallization and Water of Constitution. W. W. COBLENTZ.
22. Distribution of the Intensity of Radiation from Radioactive Substances. E. RUTHERFORD.
23. The Dispersion of Electric Waves. L. E. WOODMAN and H. W. WEBB.
24. Note on the Compound Interferometer. C. W. CHAMBERLAIN.
25. The Constancy of Platinum Thermo Elements and other Thermo-element Problems. W. P. WHITE.
26. Some Properties of Moving Coil Galvanometers. W. P. WHITE.

Adjourned.

ERNEST MERRITT,
Secretary.

NOTE ON A NEW FORM OF RADIOMETER.[1]

BY W. W. COBLENTZ.

THE chief objection to a radiometer having vanes of appreciable area is its slow period. This can be shortened by using a heavier fiber, which means a decrease in sensitiveness. This can be compensated for by increasing the efficiency of the vane. Now, in a radiometer the energy developed is at the surface of the vane, which by conduction transmits it to the surrounding medium. In the thermopile we use only the energy developed within the conducting wire.

[1] Abstract of a paper presented at the meeting of the Physical Society held April 20–21, 1906.

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The present scheme is to superpose the radiometer effect upon the radiomiaometer effect, by placing the whole in a vacuum and making the Bi-Sb or Cu-Te thermojunction the vane of a radiometer. The junction is in the form of a ⊥, part of the long side being the vane. The loop of copper wire lies in the same plane and joins two of the free ends. The magnet is taken from a Weston ammeter. In other respects the whole is similar to the Boys radiomicrometer, with the exception that the suspended system is in a vacuum, which is an added advantage since, as shown by Kurlbaum, the sensitiveness is increased in a rarified atmosphere.

On account of numerous delays and pressure of other work, it has not been possible to give the instrument a thorough test for sensitiveness. It might be added, however, that the aim is not so much to develop an instrument which is more sensitive than a radiometer, but to construct a device that for a given sensitiveness has a shorter period than obtains in an ordinary radiometer. In an ordinary radiometer the suspension weighs about 10 to 12 mg. In the present case the weight is 20 mg. The half period is only 5 sec. at present. Selecting a finer fiber would make it more sensitive.

In conclusion I might add that I hesitate to give the data for sensitiveness of the present suspension (junction of Cu-Te), because the radiometer effect is only about fifteen per cent. of the radiomicrometer while it is well known that at all times the radiometer is the more sensitive instrument. By making the suspension of lighter material the radiometer effect will be increased. The present suspension is about three times as sensitive as the radiomicrometer described by Boys.

For measuring small electric currents, *e. g.*, from telephone, etc., we obviously need not have such a large vane. The heating coil is to be placed between the vane and what corresponds to the inner window of the radiometer as it appeared in its original form. It would seem that such an instrument ought to be more sensitive than the modification of the Boys' radiomicrometer which is now being exploited under a patent.

On the Determination of Melting Points by Radiation Methods.[1]

By C. W. Waidner and G. K. Burgess.

THE methods used are based on the monochromatic and on the total radiation from platinum at different temperatures. Minute specimens of the metals to be studied are placed on a platinum ribbon whose temperature is slowly raised by an electric current flowing through it;

[1] Abstract of a paper presented at the meeting of the Physical Society held April 20–21, 1906.

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the melting is observed through a microscope, and the corresponding "black body" temperature of the platinum ribbon is observed with an optical or radiation pyrometer. From the known departure of platinum radiation from black body radiation, the true temperatures are obtained.

The platinum ribbon is mounted within an enclosure with mica window thus permitting determinations to be carried out in any desired atmospheres (air, H, N). The method is particularly applicable to the oxidizable elements, and also to the rare elements as only a few milligrams are required. Experiments with different size particles of metals of known melting points give the small correction for the temperature difference between strip and specimen undergoing melt.

The method has been applied to a study of the metals of the iron group and to palladium, and is applicable within the range 600° to 1650° C., and higher with iridium or graphite strips.

CHELTENHAM MAGNETIC OBSERVATORY REGISTRATION OF EFFECTS FROM ELECTRIC CARS OVER TWELVE MILES DISTANT.[1]

BY L. A. BAUER.

A CLOSE inspection of the magnetograms obtained during the past year at the United States Coast and Geodetic Survey Magnetic Observatory situated at Cheltenham, Maryland, employing the sensitive Eschenhagen-Edler variometers has disclosed the interesting fact that magnetic effects are being photographically registered daily which are to be ascribed to an electric car line 12 to 14 miles distant. This line proceeding from Washington to Mt. Vernon, Virginia, is a "single trolley" line with defective bonding of the rails.

The magnetic element principally affected, viz., the vertical intensity, exhibits during the period of the day (5 A. M. to about one and one half hours after midnight), when the cars are running, a number of short, more or less periodic, waves of fluctuations superimposed upon the normal curve. The average deflection to be ascribed to the electric car effect is about $\frac{1}{75000}$ to $\frac{1}{150000}$ part of the vertical intensity.

The effects are being further investigated; a fuller publication will be found in the March issue of the journal "Terrestrial Magnetism and Atmospheric Electricity."

Up to this time it had been generally supposed that no electric car effects could be detected beyond five miles.

[1] Abstract of a paper presented at the meeting of the Physical Society held April 20–21, 1906.

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A New Potentiometer.[1]

By H. B. Brooks.

MEASUREMENTS of electromotive force and current are made with two general classes of instruments. Those of the first class may be called deflection instruments, those of the second, balance instruments. Most portable voltmeters and ammeters belong to the first class, while the potentiometer is the best example of the second class. Deflection instruments are less accurate, less permanent in calibration and more affected by external disturbing forces than balance instruments; on the other hand deflection instruments are less expensive and more readily applied, and readings may be taken more rapidly than with balance instruments. The latter are preferred for precision work in the laboratory; the former for approximate work in the laboratory and for commercial work. The merits of the potentiometer method for precision work are well known.

A middle class of work calls for an accuracy better than that of deflection instruments, but not so great as that of the precision potentiometer. It also requires permanency of calibration, independence of external disturbing forces and as much as possible of the convenience and speed of working of the deflection instrument. The work to be done by such an instrument includes the calibration of deflection instruments in the factory and testing room, the checking of ammeters and voltmeters in the central station, including switchboard instruments in position, and photometric work.

To meet this need larger deflection instruments have been supplied, and also portable potentiometers. The former may be read quite closely, on account of the longer needle; they are, however, subject to all the sources of error peculiar to deflection instruments. The portable potentiometer has not fully met the need, one reason being that measurements cannot be made unless the current or voltage to be measured is quite steady, a condition not found on commercial circuits.

To meet the need above mentioned a new form of potentiometer has been devised, which measures the bulk (say from 95 to 99 per cent.) of the quantity to be measured by the potentiometer principle, the remainder being measured by deflection. Thus the sources of error peculiar to the latter affect only a small portion of the result, while the operation of the instrument is much simplified. If the current or voltage is fluctuating, the instantaneous values may be read, it being unnecessary to change the dial unless the fluctuations are very great.

The instrument is a one dial potentiometer with a calibrated galvanometer, the circuits being so arranged that the sensibility is constant, re-

[1] Abstract of a paper presented at the meeting of the Physical Society held April 20–21, 1906.

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gardless of the setting of the dial. The general expression for the galvanometer current in an unbalanced potentiometer has been derived and used as a guide in planning the circuits.

An instrument for voltage measurements on this principle has been constructed and used in the work of the Bureau of Standards. It has been found very accurate and much more convenient to use than a potentiometer of standard form. A second instrument will be constructed, in which more than one range will be provided for.

SELECTIVE REFLECTION IN THE INFRA-RED.[1]

BY A. H. PFUND.

TO begin with it is shown that the character of the selective reflection of a substance is not affected by a change of state, so long as the molecule as a whole remains unaffected. Then the curves of selective reflection from liquids are discussed — especially of sulphuric acid. These curves change markedly with changes in the concentration of the acid. The effect is attributed to the formation of new ions. Finally, it is shown that the mechanism giving rise to certain marked bands of selective reflection in the infra-red is in all probability localized in that portion of the molecule which in solution becomes the negative ion. All of the results thus far obtained (involving work on sulphates and nitrates) fully bear out the above conclusion.

POLARIZATION IN THE INFRA-RED.[1]

BY A. H. PFUND.

THE first part of the paper is taken up with a discussion as to the suitability of certain substances to act as polarizers in the infra-red. A new form of polarizer and analyzer is developed (involving the use of amorphous selenium), which has very decided advantages over existing forms. With these new instruments it is shown that Iceland spar in its region of metallic reflection transforms plane into elliptically polarized light by reflection.

[1] Abstract of a paper presented at the meeting of the Physical Society held April 20–21, 1906.

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Spectral Lines as Light Sources in Polariscopic[1] Measurements.

By Frederrick Bates.

RECENT progress in polariscopic work necessitates careful consideration of the character and behavior of the light sources used. Unless the source can be accurately defined and its constancy depended upon it is obviously impossible to compare the polariscopic measurements of different observers.

Let two spectral lines with unequal intensities be considered as a source of light for a half shade polariscope. It is found from a theoretical development that a rotation is measured which differs from the rotation that would have been obtained, had the lines been of equal intensity, by an angle

$$\delta = \pm \tfrac{1}{2} \frac{K-1}{K+1} (a_1 - a_2), \qquad (1)$$

where K is the ratio of the intensities and $(a_1 - a_2)$ is a function of the rotation dispersion.

By means of (1) we can calculate the optical center of gravity of the sodium lines and the errors in measuring rotations with these lines as the source of light.

The use of the line 546.1 $\mu\mu$ obtained from incandescent mercury vapor is advocated as the international standard source for all polariscopic measurements. In order to make possible the use of this source where the rotation value for quartz is desired in terms of the sodium lines a determination was made of the temperature coefficient and also the ratio of the rotation for the proposed source and the sodium lines.

We have thus the formula

$$a_t = a_0(1 + 0.000144t),$$

giving the rotation for quartz at any temperature between 4° C. and 50° C. for the line 546.1 $\mu\mu$. To give the rotation in terms of the sodium lines we have

$$\frac{\sigma_\lambda = 546.1}{\sigma_\lambda = 589.25} = 1.175166 \pm 0.000012.$$

[1] Abstract of a paper presented at the meeting of the Physical Society held April 20–21, 1906.

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THE ELECTROLYTIC WAVE DETECTOR.[1]

BY L. W. AUSTIN.

THE electrolytic wave detector first described by Fessenden and later independently by Schlomilch consists essentially of a cell having as one electrode a point of fine platinum wire and containing an electrolyte the decomposition products of which are gaseous. When an E.M.F. is applied to such a cell powerful polarization ensues so that practically no current passes unless the E.M.F. exceeds a certain value. When electrical oscillations pass through the cell this resistance is for the time decreased but returns to its former value as soon as the waves cease.

This work was undertaken with the purpose of gaining some quantitative data regarding the detector and with the hope of settling some of the disputed points regarding its action. Experiments were made with the cell excited by alternating currents of low frequency and also by true electrical waves supplied for the most part from a station seven miles away. The action in the two cases seems to be in general the same.

The following are the principal results:

When the polarization is complete enough so that a sensitive galvanometer can be used, a few thousandths volts alternating E.M.F. can be detected.

The decrease in the resistance of the cell is approximately proportional to the square of the applied alternating E.M.F.

With increasing polarizing E.M.F. the sensitiveness increases to a maximum after which it remains constant or decreases.

Under favorable conditions the cell is found to be about equally sensitive with positive (oxygen) or negative (hydrogen) polarization on the point thus supporting the results of Fessenden and Rothmund and Lessing in opposition to those of DeForrest and Schlomilch. At times however the action with negative polarization is irregular, the resistance occasionally increasing instead of decreasing.

The resistance of the cell is very variable depending on the polarizing E.M.F. When the polarizing E.M.F. is low it may be 50,000 ohms or more while at the point where the polarization is beginning to break down it is sometimes less than 1,000 ohms. In the case of rapid oscillations the effective resistance is modified by the fact that the cell acts as a condenser.

For slow alternations the cell is equally sensitive whether the small electrode is minute or of considerable size. For oscillations of the period usually used in wireless telegraphy the area should not exceed 0.0003 mm. This difference in action is probably due to the capacity effect of the point.

[1] Abstract of a paper presented at the meeting of the Physical Society held April 20–21, 1906.

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In order to test the hypothesis that heat is a prominent factor in breaking down the polarization resistance at the small electrode, this electrode was made in the form of a loop of wire through which an alternating heating current could be passed. It is found that the heating of the electrode produces a marked diminution in the resistance of the cell, which indicates that heat is at least one of the factors in the phenomenon.

On the Influence of Frequency Upon the Self-Inductance of Cylindrical Coils of any Number of Layers.[1]

By J. G. Coffin.

CALCULATIONS on a marble standard of self-inductance, constructed for the Bureau of Standards, showed that a change in the self-inductance with the frequency, of over 0.25 per cent., was possible.

In accurate work, this is a very large variation and it is necessary to derive a method for assigning the correction to be applied to any given coil at any given frequency.

Such a method is given in this paper, which is an extension of one for the corrections to a coil of a single layer, shortly to be published in the Bulletin of the Bureau of Standards.

Starting from Maxwell's equations, a differential equation is derived for the variation in the magnetic field as a function of the distance from the central axis of the coil, with any frequency.

The solutions of this equation are the Bessels functions of the zeroth order. Following A. Sommerfeld, these solutions are replaced by approximation formulæ, thus reducing the problem to one in simple functions alone.

An equation is then derived which gives the law according to which the variable part of the self-inductance of a coil of m-layers changes with the frequency.

Curves are drawn which render the calculations for any given coil very easy. Approximation formulæ for the case of low and high frequencies are also derived.

This paper will appear in a future number of the Physical Review.

[1] Abstract of a paper presented at the meeting of the Physical Society held April 20–21, 1906.

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ON THE GEOMETRIC MEAN DISTANCES OF SQUARE AREAS, AND THEIR USE IN THE CALCULATION OF SELF AND MUTUAL INDUCTANCES.[1]

BY EDWARD B. ROSA.

MAXWELL gave the value of the geometric mean distance of two adjacent squares (*Trans. Royal Soc. Edinburgh*, 1871) as .99401 times the distance between their centers, and the geometric mean distance of two squares corner to corner as 1.0011 times the distance between their centers. From this he calculated the correction to be applied to the self-inductance of a coil of round wire of rectangular section to make allowance for the difference in the mutual induction of round wires on one another from the mutual induction of square wires. This correction is $-4\pi na \times .01971$ cm. (*Elec. and Mag.*, II., Par. 693). Stefan stated (*Wied. Am.*, 1884) that Maxwell's value was wrong, and gave the correction as $+4\pi na \times .01688$ but did not show how he got this value or wherein Maxwell's figure was wrong.

I have worked out the geometric mean distances of neighboring squares and find Maxwell's values wrong. For adjacent squares the figure is 1.00655 instead of .99401, and for squares corner to corner it is .997701 instead of 1.0011. The correction ΔM is therefore positive instead of negative as given by Maxwell, and its numerical value is never as great as that given by Maxwell. It is, however, not a constant (as stated by Stefan) but varies with the number of turns of wire in the coil and the shape of the cross section.

It is .01075 (multiplied by $4\pi na$) for a coil of four turns, 2×2, .01515 for 16 turns, 4×4, and has a limiting value of .01806 for a large number of turns.

Values of the geometric mean distances are deduced for 20 different squares situated in one quadrant from a given square. These are also of value in calculating the mutual inductances of parallel coils near each other.

MICA CONDENSERS AS STANDARDS OF CAPACITY.[1]

BY E. B. ROSA AND F. W. GROVER.

THE use of mica condensers as standards of capacity is justified by the most careful examination of their behavior. The capacity is not, however, perfectly constant, and in order to know the capacity at any given time it is necessary to know certain characteristic constants.

[1] Abstract of a paper presented at the meeting of the Physical Society held April 20–21, 1906.

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That is, in addition to the capacity accurately determined under standard conditions we should know:

1. The temperature coefficient of the condenser. The coefficient is usually constant for a limited range of temperature, but it begins to increase rapidly at 25° to 30° C. in some condensers. It is therefore necessary to investigate the temperature variation carefully when the condenser is to be used at different temperatures.

2. Variation with time of charge and discharge, or frequency of current if subject to periodic electromotive force. As condensers are used in a variety of ways, it is necessary to know how the capacity varies with the method and rapidity of charge and discharge.

3. Variation with the potential used, that is, with the electric stress on the dielectric. The change of capacity with the potential employed is usually inappreciable, but is sometimes considerable.

4. The power factor of the condenser is an indicator of its quality. The best condensers have extremely small (but measurable) power factors; yet some condensers made for standards show quite large power factors. The power factor depends both on leakage and absorption. The latter must be small when the power factor is small.

Results of measurements of these various quantities for several condensers will be given, as well as some of the methods employed in the measurements.

The Ratio of the Electromagnetic and Electrostatic Units.[1]

By E. B. Rosa and N. E. Dorsey.

ALTHOUGH this ratio has been determined by various investigators, their results do not give its value to within one part in a thousand, as there are considerable differences in the values obtained. We have been carrying out a series of investigations for nearly two years in order to determine its value at least to 1 part in 5,000, and hope to fix its value to within 1 in 10,000.

In order to give as great weight as possible to our result, we have employed more than one apparatus and more than one method, and have varied the working conditions in many ways. The following are some of the main features of the work:

1. We have used the condenser method, getting the capacity of condensers by calculation from their dimensions and their electromagnetic capacity by rapidly charging and discharging them. This method is undoubtedly superior to any other for accurate work, being probably the only method capable of high accuracy.

[1] Abstract of a paper presented at the meeting of the Physical Society held April 20–21, 1906.

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2. We have used three forms of condensers, spherical, cylindrical and plane. The spherical has two inner balls, giving two different capacities; the plane has one plate movable, giving a variety of capacities. The spherical requires no guard ring, is the simplest form, but requires careful determination of the capacity of the charging wire which protrudes through a hole in the outer shell. The plane and cylindrical condensers have guard rings, but are simpler with respect to the capacity of the charging wire. Using such a variety of forms and sizes of condensers gives a thorough test as to any errors that might remain as constant errors in a determination with a single instrument.

3. The electrostatic capacities have been determined with the greatest care, using standards of length and mass in so doing that have been calibrated by reference to the standards of the Bureau of Standards.

4. The electromagnetic capacities have been determined by two separate methods, (1) the Maxwell bridge method and (2) a differential galvanometer method. In the latter case the charges were sometimes measured and at other times the discharges. No differences could be detected between these, and the bridge and differential methods have also agreed.

5. The resistances used have been in oil, they have been carefully standardized, they have been used at various temperatures, different boxes have been employed for a given purpose and every precaution taken to discover sources of error and to eliminate accidental errors.

The apparatus employed in this work will be exhibited and the results so far obtained will be given. The mean value of all the measurements is about 2.9961×10^{10}.

WATER OF CRYSTALLIZATION AND WATER OF CONSTITUTION.

BY W. W. COBLENTZ.

MANY chemical compounds contain both oxygen and hydrogen, which, on applying heat, pass off in the form of water. The manner in which the water exists in minerals of this kind is not understood. By some it is considered a part of the chemical molecule; by others it is thought that the molecules of water exist in their entirety among the other molecules which constitute the compound. From the circumstance that many of these compounds are crystalline, the water is said to be present as "*water of crystallization.*" It is a characteristic of water of crystallization that it is expelled at a temperature far below red heat and frequently below 100° C.

On the other hand, the water which is given off only at a red, or even a white heat, can scarcely be present in the compound in the same man-

[1] Abstract of a paper presented at the meeting of the Physical Society held April 20–21, 1906.

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ner as water of crystallization and is distinguished as "water of constitution." In this case, the water is not supposed to exist as such in the mineral, but to result from the union of oxygen or hydrogen, or from the hydroxyl groups contained in the compounds. The whole question is in an unsettled state, while the data bearing upon it is almost *nil*.

In a preliminary paper[1] bearing upon the subject, the writer described the infra-red absorption spectra of two minerals, selenite, $CaSO_4 + 2H_2O$, and brucite, $Mg(OH)_2$ in which the atoms of oxygen and hydrogen are thought to be combined in a different manner.

It was the application of the results of the previous work in which it was abundantly proven that certain groups of atoms have characteristic absorption bands. Hence, if the oxygen and hydrogen, which enter into the composition of certain minerals, are bonded as they are in a molecule of water, then one would expect to find the absorption spectra of such minerals to be the composite of the bands of ordinary water and of the bands due to the other constituents. In the previous paper, selenite and brucite were selected as characteristic examples. They confirmed the theory in a broad sense, but two minor details needed further inquiry. First, the water band at $4.75\,\mu$ was too deep in selenite for the thickness of the plate examined, and in addition, it was shifted to $4.65\,\mu$. This would suggest that the band is complex. From its great depth and from the behavior of the sulphur compounds in this region, it was surmised that the band might be due to SO_4 radicle.

In the second place, the OH radicles in brucite contradicted other work in which it was found that the hydroxyl group causes an absorption band at $3\,\mu$. For these and other reasons it was deemed worth while to give the subject a thorough investigation.

For reasons too extensive to be discussed here, the minerals were examined in unpolarized light. The infra-red absorption spectra were examined by means of a large mirror spectrometer, a rock salt prism and a Nichols radiometer. The chief difficulty encountered was in obtaining suitable minerals, which were then ground to a thickness of about 0.1 mm. Over a hundred minerals have been examined, the majority having oxygen or hydrogen. As yet, the results have not been thoroughly worked out.

The exceptions to the rule that minerals containing water of crystallization should show water bands are but few, and belong to the group which is in doubt by mineralogists. At least thirty minerals containing water of crystallization were examined. In the same manner, the exception to the rule that minerals containing water of constitution should *not* show water bands is confined to cane sugar, which in all forms, from amorphous to crystals of rock candy, shows water bands. From com-

[1] PHYSICAL REVIEW, 20, p. 252, 1905.

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parison with dextrose, maltose and lactose, it would contain one molecule of water crystallization.

The list of sulphates examined is extensive and gives concordant results in showing a band at 4.55 μ due to the SO_4 radicle.

In the silicates, as well as in many other compounds, the general absorption increases beyond 5 μ. The maxima of the metallic reflection bands and the same determined from the transmission curves do not always coincide.

A series of hydroxides show a band at 3 μ. Brucite is *not* an exception to the rule for hydroxyl groups. Using a larger dispersion and a very much thinner film, the large band at 2.6 μ is now found to be complex with maxima at 2.5, 2.7 and 3 μ.

In quartz the first band is found at 2.9 μ. This is followed by pairs of bands at 5.0–5.3, 5.95–6.22, 8.49–9.03 and a wide band at 20.75 μ.

In the silicates studied the first band is at 2.85 or 2.91 μ, while the following ones may be at 5.6 μ and at 5.95 or 6.22 μ (sometimes both are present). Beyond this point the opacity is too great to extend observations.

The micas are known to have pairs of "reststrahlen" bands at 8.32–9.38 and 18.4–21.25; the latter being represented in quartz by the band at 20.75 μ.

On first consideration these bands seem harmonic. If we take the difference of the reciprocals of the wave-lengths of the pairs at 2.85–2.91, 5.95–6.22, 8.49–9.03 and 18.4–21.25 μ, we find that the value, in whole numbers, is from 70 to 72 which would indicate a spectral series of doublets. While not much reliance can be placed upon such results considering the present state of our knowledge, the relations indicated are very suggestive. In view of this fact, with the accumulation of minerals at hand, it is hoped to extend the work by means of metallic reflection using a bolometer and a wire grating. The most important minerals have been examined to 12 μ by means of (metallic) reflection and it will be sufficient to add that the sulphates have a series of reflection bands at 8.1 to 9.1 μ beyond which they again become transparent. The band at 9.1 μ is harmonic with the absorption band at 4.55 μ. The reflection band at 8.7 μ which is marked in the sulphates examined, viz., Ca, Mg, Ba, Sr and Na, is the strongest absorption band in SO_2. As a whole it appears that the SO_4 radicle can be added to the list[1]: viz., CH_3, NH_2, C_6H_5, NO_2, OH and NCS, which have characteristic absorption bands in the infra-red. The silicon radicle is still in doubt.

BUREAU OF STANDARDS,
WASHINGTON, D. C.

[1] PHYS. REV., 20, p. 362. 1905.

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Some Properties of the Moving Coil Galvanometer.[1]

By Walter P. White.

By combining equations (1), (5), (13) and (16), of the author's article on sensitive moving coil galvanometers,[2] we obtain the equation

$$H = A\sqrt{\frac{R}{R'T}}, \qquad (1)$$

where R is the critical resistance, R' the resistance of the coil, T the full undamped period, and H the mean effective field strength in c.g.s. units. A is constant on the assumption used in obtaining the original equations — namely, that all inert material in the coil can be neglected. It is, however, constant in any case for the same coil, it varies within rather narrow limits (from 600 to 800) for such coils as are ordinarily used, and can be estimated within ten per cent. from the dimensions and appearance of the coil. Therefore,

1. This equation gives a simple method for measuring the effective field strength of the magnet of a galvanometer without removing the coil from the case, and without knowing the size of wire or the number of turns in the coil.

2. Our ability to obtain short periods depends on the magnet and the internal and external resistance, regardless of the sensibility or the mass of the coil.

3. In applying the above equation to a copper damping frame, $R/R' = 1$ and A, on account of the absence of insulating material, is lower, varying from 425 to 500. This case gives the lowest value of $A\sqrt{R/R'}$ obtainable with copper. Hence the shortest possible period for any kind of a copper coil whatever is given by the equation

$$H = \frac{425}{\sqrt{T}}. \qquad (2)$$

For aluminum, $H = 236/\sqrt{T}$.

4. For a coil whose damping is partly due to a copper or aluminum frame, the minimum period lies between the values proper to the frame and to the coil; but obviously, it will always be greater than that given by equation (2). The equation for this case is

$$H = A\sqrt{\frac{R}{R'T}}\sqrt{\frac{D + d\frac{R'a^2}{RA^2}}{D + d}},$$

[1] "Sensitive Moving Coil Galvanometers," Physical Review, 19, 305. 1904.

[2] Abstract of a paper presented at the meeting of the Physical Society held April 20–21, 1906.

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where D is the damping coefficient of the coil, d that of the frame, and a the value of A for the damping frame.

The detrimental magnetic effect is proportional to the magnetic attraction divided by the controlling force; that is, to H^2K/Q, if the shape and manner of construction of the coil do not vary. By the use of equation (1), it can then be shown to be proportional to TR/R'; that is, zero shifts, etc., are in general less troublesome at short periods.

The Constancy of Platinum Thermoelements, and Other Thermoelement Problems.[1]

By Walter P. White.

I.

It has frequently been observed that thermoelements of metals of the platinum group deteriorate when exposed at 1200° or even less in a reducing atmosphere. The trouble has been variously attributed to reduced silicon or absorbed gases, but appears not to have been thoroughly investigated. It is usually removed by sufficient heating of the wires in air. At this laboratory, much trouble has been experienced from contamination of a character totally different and apparently hitherto unrecognized. It occurs at higher temperatures (1000 to 1600°), in an oxidizing atmosphere, and is much more serious.

The total thermoelectromotive force in any circuit equals $\int TdH$, where T is the temperature above that of the cold junction, and H is the thermoelectric height. In a thermoelement which is not homogeneous, therefore, the reading depends on a large number of different temperatures, namely, those at every point at which there is a change in the character of the wire. The reading of the contaminated elements, therefore, varied irregularly, according to the accidental condition of the furnace in which they were placed. It was found possible, however, to work with such elements by comparing them frequently with standards, taking great pains to make the comparison under conditions of temperature distribution in the furnace as nearly as possible the same as those prevailing when the elements were used to read temperatures. The standards were in use only a few minutes each day, and therefore deteriorated with relative slowness. At 1400° results obtained by this method generally agree within one third of a degree.

An investigation into the cause of the trouble, with a view to its prevention, began with the physical study of the contaminated wire, that is, of its thermoelectric properties.

[1] Abstract of a paper presented at the meeting of the Physical Society held April 20–21, 1906.

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Several different forms of apparatus were tried. Their general principle is the following: The wire to be tested was in contact at two points, *A* and *B*, one or two centimeters apart, with two lead wires of the same material which ran off to a cold junction. *A* was heated indirectly by means of steam, while *B* was kept cool. The wire between *A* and *B* thus formed part of a thermoelement; and its thermoelectric height compared to the lead wires, and therefore the amount of its deterioration, could be easily found. Since all the wires were of the same material, the method was a differential one, and slight inequalities of temperature in the circuit, as well as small changes in the difference of temperature beween *A* and *B*, did little harm. In the apparatus that was found best for general work, *A* and *B* were over and insulated from plates of copper. For one or two special investigations a sharper temperature gradient was obtained by using two baths of kerosene, each containing a stirrer, and separated by a thin wooden partition through which the wire passed.

With the testing apparatus it was possible to get not only more definite results than could be obtained by the observation of thermoelements in furnaces, but to work on pieces of wire 2 or 3 cm. long, which could easily and at slight expense be subjected to various conditions. The investigation then undertaken yielded the following results:

1. The contamination of the platinum wire causing the change in electromotive force probably represents in the worst cases two or three per cent. of added impurity.

2. The platinum-rhodium wires are altered in electromotive force about one fourth as much as the platinum, which probably indicates an equal percentage of added impurity.

3. The contamination is first noticed at about 1000° and increases with the temperature. (Of course it also increases with the time.)

4. Only a little of the contaminated material is removed by glowing, that is, heating the wires nearly to their melting points by an electric current.

5. Wires heated in carbon monoxide and illuminating gas under a wide variety of conditions showed no contamination at high temperatures, 1200° and above.

6. Wires heated to 1500° for an hour in a glazed porcelain tube showed no contamination; no contaminating substance came through the furnace, and the porcelain gave out none. There is therefore probably no danger of contamination from silicates in an oxidizing atmosphere.

7. A platinum wire in a porcelain tube with a wire containing ten per cent. of iridium showed about as much contamination as when used in the furnace. Iridium from the coils of our furnace, which contain ten per cent. of it, is therefore probably the main cause of the trouble we have experienced.

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8. Chemical analysis showed iridium in substantially the expected amount.

9. A few milligrams of iron wire inserted in the tube caused contamination. The wire probably exhausted the oxygen in the tube when first put in.

10. Ferric oxide at the same temperature (1500°) produced no contamination.

11. The wires were not contaminated in front of a blast lamp, but they were in the exhaust from a Fletcher furnace. Iron in some form was found to be present in the gases from this furnace, which also probably gave at times a reducing atmosphere.

12. When a tube of commercial platinum was used to shield the test wire from the furnace atmosphere, the wire was still contaminated. When the tube itself was tested thermoelectrically, it was found to contain at least three or four per cent. of impurity. As much of this was probably iridium, its presence is believed to be the cause of the contamination obtained with this tube. Thermoelectric tests of other samples of commercial platinum show from one half of one per cent. of iridium upward. Proximity to commercial platinum is therefore a source of danger to thermoelements at high temperatures.

13. A Heraeus thermoelement from the Corning Glass Works, which had been in continuous use for five months at 1400° in gas furnaces, showed one or two per cent. contamination of the platinum wire; far less in proportion to the time than was shown by our elements. But a striking difference was found in the condition of the rhodium-alloyed wire, which was not contaminated at all. A chemical test is now in progress to see whether the contamination in this case was due to rhodium from the rhodium wire.

14. Two attempts to check the contamination of wires by the use of a nitrogen atmosphere have failed. Further work, however, will be done in this direction.

CONCLUSION.

The proximity of platinum containing iridium, etc.; that is, practically all commercial platinum, will cause deterioration of platinum thermoelements when exposed in an oxidizing atmosphere above 1000°. There is apparently no other source of danger in an oxidizing atmosphere.

II.

Ordinary wires of constantan, German silver, etc., show inhomogeneities which greatly detract from their value in thermoelectric work. By using a thermopile instead of a thermoelement, the total electromotive force was increased and at the same time it was hoped that the inhomo-

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geneities would tend to neutralize each other's effect. Experience seemed to show that it was better to first test the condition of the wire rather than rely on accidental corrections. A wire tester adapted to insulated wires several meters in length was made of a steam-jacketed glass tube. The wire was gradually drawn out of this tube, so that the thermoelectric height of the portion which was at the opening at any time was compared directly with another immovable portion. The result showed for No. 36 Advance wire a rise and fall of thermoelectric height with a fairly constant period of 60 cm., averaging about .25 per cent. of the electromotive height against copper, or over ten times the height of the short period variations found by Professor Hall.[1]

GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION,
WASHINGTON, D. C., April, 24, 1906.

THE VELOCITY, AND RATIO e/m, FOR THE PRIMARY AND SECONDARY β-RAYS OF RADIUM.[2]

BY S. J. ALLEN.

THE work of Kaufmann has shown that the primary β-rays are composed of negatively charged particles travelling with velocities nearly equal to that of light, and that further, as the velocity of light is approached the apparent mass of the electron increases rapidly. In trying to repeat these results, using, instead of the photographic method of Kaufmann, the well-known ionization one, the author experienced at first great difficulty in getting any true deflection of the β-rays. By further investigation however this difficulty was shown to be due to the presence of secondary and tertiary rays, which to a great extent masked the action of the primary β-rays.

An investigation into the nature of these secondary and tertiary rays, more especially absorption tests, and their behavior in a magnetic field, brought forth the following facts:

1. When the β-rays strike upon solid objects, there is produced at the surface of these, secondary rays, which differ both in quantity, and penetrating power with the nature and density of the object.

2. Nearly all of the secondary rays, whether from dielectrics or metals, are deflected in a magnetic field in the same direction as the primary β-rays would be.

[1] Proc. Am. Acad., 41, 543.

[2] Abstract of a paper presented at the Washington Meeting of the Physical Society, April 21, '06.

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3. The penetrating power of secondary rays is greater for the substances of high density, but in any case it is not much less than the medium and slow velocity primary rays.

4. When the secondary rays in turn strike upon solid objects, there is produced a third type of rays similar in all respects to the secondary rays, but of slightly less penetrating power.

5. The amount of secondary rays produced by the γ-rays is small compared with that produced by the β-rays, but is of the same general nature. From these results an explanation of the difficulty experienced at first by the author can at once be obtained.

When a beam of β-rays, cut down to a supposed narrow width is allowed to fall upon the window of an electroscope of width the same as that of the incident beam, then besides this beam of β-rays there is also present a diffuse beam of secondary and tertiary rays, which as has just been shown are of the same general nature as the β-rays themselves, *i. e.*, deflectable in a magnetic or electrostatic field. Consequently the deflection of the β-rays would be very much confused by the accompanying deflection of the secondary and tertiary rays, so that an apparent total deflection of some 30 per cent. might mean more than complete deflection of the primary rays.

This difficulty was removed by the following method which proved successful.

The beam of β-rays was just prevented from entering the electroscope window by a suitable screen. Now it was found that, when the magnetic or electrostatic field was applied in such a direction as would bend the rays into the window, the ionization in the electroscope gradually increased to a maximum with increasing fields. When this maximum point had been reached for either the magnetic or electrostatic fields, the β-rays of least velocity had just been bent across the electroscope window. Knowing the strengths of the magnetic and electrostatic fields necessary to produce this maximum ionization, the velocity of the least penetrating ray could at once be calculated. By interposing in the path of the rays suitable layers of absorbing material, the velocity of the least penetrating ray which could just get through the absorbing layer could be ascertained. The effect of the secondary and tertiary rays was to change the amount of the increase of ionization but not the maximum point.

The experiments were performed in a high vacuum, the rays emerging from the vacuum vessel through a thin sheet of mica.

The velocity of the secondary rays was obtained in exactly the same manner, the radium being enclosed in a lead box which cut off all the primary rays and allowed only the secondary rays to pass out through a small opening. The complete results for both primary and secondary rays are given in the following table:

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Primary β-Rays.

Absorbing Layer.	X (max.).	H (max.).	mv/e	V cm./sec.	e/m
0	—	—	1.57×10^{3}	2.20×10^{10}	1.40×10^{7}
6 sheets paper.	5.7×10^{11}	13.5	1.87	2.37	1.27
10 " "	6.1	14.3	1.98	2.40	1.21
14 " "	6.6	15.1	2.10	2.45	1.17
18 " "	7.2	16.2	2.25	2.49	1.10
22 " "	7.7	17.0	2.36	2.54	1.07
30 " "	8.3	17.9	2.49	2.60	1.04
1.5 mm. glass.	9.6	20.0	2.78	2.69	.96
.3 " copper.	11.0	22.2	3.09	2.77	.90
.4 " zinc.	14.0	27.2	3.79	2.88	.76
.8 " "	—	—	4.60	2.95	.64
1.2 " "	—	—	5.00	2.97	.59

Secondary Rays from Lead.

0	—	—	1.56×10^{3}	—	—
6 layers paper.	6.9×10^{11}	16.0	1.85	2.35×10^{10}	1.27×10^{7}
14 " "	7.5	17.0	1.97	2.40	1.21
22 " "	8.5	18.5	2.16	2.50	1.16
30 " "	9.6	20.2	2.36	2.58	1.09

Is will be seen at once from these tables that the limiting velocity of the rays for the same thickness of material is the same for both primary and secondary radiations. The values of the velocity, and ratio e/m, for the rays are very close to those found by Kauffman, and lend additional weight to the view that the mass of the election is entirely electrical in nature. The fact is also brought out in this investigation that the secondary rays are of the same nature as the primary β-rays, and travel at nearly the same velocity.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MD.,
April 26, 1906.

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